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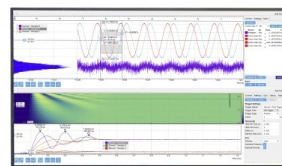
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Calculation of electric quadrupole linestrengths for diatomic molecules: Application to the H₂, CO, HF and O₂ molecules

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We present a unified variational treatment of the electric quadrupole (E2) matrix elements, Einstein coefficients, and line strengths for general open-shell diatomic molecules in the general purpose diatomic code DUO. Transformation relations between the Cartesian representation (typically used in electronic structure calculations) to the tensorial representation (required for spectroscopic applications) of the electric quadrupole moment components are derived. The implementation has been validated against accurate theoretical calculations and experimental measurements of quadrupole intensities of ¹H₂ available in the literature. We also present accurate electronic structure calculations of the electric quadrupole moment functions for the $X^1\Sigma^+$ electronic states of CO and HF at the CCSD(T) and MRCI levels of theory, respectively, as well for the $a^1\Delta_g - b^1\Sigma_g^+$ quadrupole transition moment of O₂ with MRCI level of theory. Accurate infrared E2 line lists for ¹²C¹⁶O and ¹H¹⁹F are provided. A demonstration of spectroscopic applications is presented by simulating E2 spectra for ¹²C¹⁶O, H¹⁹F and ¹⁶O₂ (Noxon $a^1\Delta_g - b^1\Sigma_g^+$ band).

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I. INTRODUCTION

The electric dipole approximation is often used to treat the spectra of diatomic, or small polyatomic, molecules. For most systems, this is a valid approximation that produces good results. For homonuclear diatomic molecules however, electric dipole (E1) selection rules forbid pure rotational and vibrational transitions, as well as parallel electronic transitions and electric quadrupole (E2) transitions and magnetic dipole (M1) become important.^{1–14}

This has implications for the spectra of several important molecules. The most famous example is the hydrogen molecule, which despite being the most abundant molecule in the Universe has no infrared electric dipole spectrum. The three lowest lying electronic states of another important molecule, O₂, all have the same (*gerade*) symmetry and transitions between them are therefore electric dipole forbidden.^{5,15,16} Oxygen’s significant absorption in the visible region comes from the electric quadrupole and magnetic dipole moments.

Even when electric dipole transitions are weakly allowed through interactions with other electronic states, E2 and M1 transitions may still be detectable, and their consideration is necessary for an accurate description of the molecule’s spectrum,^{17–20} such as for the Cameron bands ($a^3\Pi - X^1\Sigma$) and fourth positive system ($A^1\Pi - X^1\Sigma$) of CO.^{18,21,22}

E2 and M1 transitions prove difficult to measure experimentally, owing to their weak intensity and the long path lengths required for appreciable absorption. Electric quadrupole transition intensities are on the order of $10^6 - 10^9$ times smaller than electric dipole transition intensities.^{19,20,23} Nevertheless, they are often present in atmospheric spectra, where sufficiently long path lengths are regularly achievable, and play an important role in geophysical and astrophysical applications.^{3–5,22,24,25}

In spectroscopic applications, as used in e.g. the HITRAN database,²⁶ the E2 intensities are usually represented by expressions in terms of effective electric quadrupole moment constants with the rotational line intensities modelled via Hönl-London factors.^{5,27} Examples of variational methodology used for electric quadrupole intensities of open-shell diatomics molecules include earlier works by Chiu²⁸, Balasubramanian, D’Cunha, and Rao²⁹, Balasubramanian and Narayanan³⁰.

Exoplanetary atmospheric retrievals require high resolution molecular opacities across a wide spectral range for a variety of temperatures. This has been the ongoing focus of the ExoMol database, and to date molecular line lists have been produced for more than

80 molecules and 190 isotopologues.³¹ However, several important homonuclear molecules, including N_2 ,³² S_2 and the crucial biosignature molecule O_2 ³³⁻³⁷ have evaded rigorous treatment, due to the dipole-forbidden nature of their spectra. As a result, these molecules are currently missing from analyses of atmospheric spectra of hot exoplanets, representing a significant obstacle to the characterisation of exoplanet atmospheres or indeed any high temperature environments.

Here we present a formulation of the electric quadrupole line intensities for a general (open-shell) diatomic molecule and an implementation of these E2 matrix element and linestrength expressions in the DUO program³⁸ - a powerful rovibronic variational program developed as part of the ExoMol project to solve the time-independent Schrödinger equations and compute rovibronic spectra of diatomics. To the best of our knowledge, this work represents the first general computational methodology for generating quadrupole spectra of arbitrary diatomic systems from first-principles, which lays the foundations for future work to produce a complete molecular line list for O_2 and other homonuclear diatomics.

The structure of the paper is as follows. Section II introduces the rovibronic basis used by the DUO program before presenting expressions for the electric quadrupole matrix elements, linestrengths and Einstein coefficients, for a general case of an arbitrary diatomic molecule. We also show how the matrix element components in the Cartesian representation, commonly employed in electronic structure calculations, are related to the tensorial representation used by DUO, and outline the approach taken to reconstruct the transformation between the two. In section III we provide demonstrations for the DUO implementation of electric quadrupole linestrength calculations, including a validation against accurate theoretical and experimental linestrengths for H_2 . We also present accurate quantum chemistry calculations of the electric quadrupole moment functions for CO and HF molecules, as well as infrared transition linestrengths for CO and HF molecules calculated using DUO. These line lists are included into the ExoMol data base www.exomol.com, which aims to provide molecular spectroscopic data for studies of exoplanetary and other atmospheres. More challenging nuclear motion applications of electronic E2 spectra of open-shell diatomic molecules are underway. As an illustration of an open-shell application, an E2 spectrum for the electronic system $a^1\Delta_g - b^1\Sigma_g^+$ (Noxon band) of O_2 is presented and compared to a experimental spectrum from the literature. The spectroscopic model for each molecule, including *ab initio* electric quadrupole moment functions $\Theta(r)$ is made available in the supplementary

material via DUO input files. We also provide a list of calculated state energies and quantum numbers, as well cross-sections and line positions in the form of ExoMol line lists.³¹

II. THEORETICAL BACKGROUND

A. Matrix Elements and Linestrengths

1. Rovibronic wavefunctions

We consider a calculation of electric quadrupole spectra for an arbitrary diatomic molecule between some generic rovibronic states. Our aim is to implement an E2 spectra module as part of the general diatomic code DUO.³⁸ The original DUO program and its methodology is detailed extensively by Yurchenko *et al.*³⁸. For the purpose of defining the matrix elements here, it suffices to simply introduce the definition of the quadrupole moment, the basis functions and the final eigenstates used by the DUO program. DUO uses the Hund's case (a) basis set in the following form:

$$|\varphi_i\rangle = |\xi\Lambda\rangle |S\Sigma\rangle |\xi v\rangle |J\Omega M\rangle \quad (1)$$

where J is the total angular momentum, M is a projection of J on the laboratory Z -axis in units of \hbar , S is the total electronic spin angular momentum, Σ is the projection of the spin of electrons on molecular z -axis, ξ are indexes of the ξ -th electronic state, Λ is the projection of the electronic angular momentum on molecular z -axis, $\Omega = \Lambda + \Sigma$ (projection of the total angular momentum on molecule z -axis) and v is the vibrational quantum number.

The eigenfunctions corresponding to the final rovibronic eigenvalues are expressed as linear combinations of the basis functions in Eq. (1):

$$|\psi_{JM\tau}\rangle = \sum_{\xi\Lambda S\Sigma v\Omega} C_{J\tau}(\xi\Lambda S\Sigma v\Omega) |\xi, \Lambda\rangle |S\Sigma\rangle |\xi, v\rangle |J\Omega M\rangle \quad (2)$$

where $C_{J\tau}(\xi\Lambda S\Sigma v\Omega) = C_{J\tau}(\varphi)$ are expansion coefficients obtained by solving a system of coupled rovibronic Schrödinger equations variationally, and τ is the symmetry of a rovibronic eigenstate. In case of a heteronuclear diatomic, τ is a parity $\tau = -$ (odd) or $+$ (even),³⁹ which reflects how $|\psi_{JM\tau}\rangle$ transforms upon inversion or, equivalently, reflection through the molecule-fixed xz plane. For a homonuclear molecule, the symmetry τ includes the parity with respect to the permutation of the nuclei and is traditionally represented by the

combinations $+/-$ (xz -reflection) as well as the g/u parities (molecular-fixed inversion), where g and u stand for ‘gerade’ and ‘ungerade’. Generally the good quantum numbers are the total angular momentum J , the symmetry τ and the g and u parities (homonuclear molecules). It is also common to assign other quantum numbers according to the largest coefficient $C_{J\tau}(\varphi)$ in the basis set expansion.³⁸

2. Electric Quadrupole Matrix Elements

The Einstein A coefficient for an E2 transition between a lower state i and an upper state f is given in SI units, by:

$$A_{fi} = \frac{8\pi^5 \nu_{fi}^5}{5\epsilon_0 h c^5} \frac{1}{(2J_f + 1)} S_{fi} \quad (3)$$

where ν_{fi} [s^{-1}] is the transition frequency, ϵ_0 [Fm^{-1}] is the permittivity of free space, h [$J s$] is Planck’s constant, c [ms^{-1}] is the speed of light in a vacuum, and

$$S_{fi} = \left| M_{fi}^{(E2)} \right|^2 = \sum_{\alpha, \beta = x, y, z} |\langle \psi_f | Q_{\alpha\beta} | \psi_i \rangle|^2 \quad (4)$$

is the transition linestrength with unit [$C^2 \cdot m^4$] and the matrix elements are those of the quadrupole operator $Q_{\alpha\beta}$ ($\alpha, \beta = x, y$ or z) defined relative to the nuclear centre of mass by

$$Q_{\alpha\beta} = -\frac{3}{2} \sum_i e_i \left(r_{i,\alpha} r_{i,\beta} - \delta_{\alpha\beta} \frac{1}{3} r_i^2 \right), \quad (5)$$

where the sum runs over the nuclei and electrons with e_i being the charge of the particle and r_i its position vector in the molecule-fixed frame. We use the common convention of Buckingham⁴⁰, used by many quantum chemistry programs such as Werner *et al.*⁴¹. Different sources employ definitions of the quadrupole moment with varying constant pre-factors, such as Truhlar⁴².

The DUO rovibronic wavefunctions $|\psi_{JM\tau}\rangle$, and the transition linestrength in Eq. (4) are defined in the laboratory-fixed frame. Meanwhile, the electric quadrupole moments in Eq. (5) are defined in the molecule-fixed frame. For the convenience of calculating matrix elements, the relationship between the molecule-fixed and laboratory-fixed components of tensor operators is best established using the algebra of irreducible tensors. Traceless symmetric quadrupole tensor of rank 2 can be expressed in terms of three irreducible tensors $Q^{(0)}$, $Q^{(1)}$ and $Q^{(2)}$ with ranks zero, one and two respectively. The components $Q_m^{(k)}$

with $-k \leq m \leq k$, are expressed in terms of the Cartesian Q_{ij} via the following standard relations:^{23,43}

$$Q_0^{(0)} = -\frac{1}{\sqrt{3}} (Q_{xx} + Q_{yy} + Q_{zz}) \quad (6)$$

$$Q_0^{(1)} = \frac{i}{\sqrt{2}} (Q_{xy} - Q_{yx}) \quad (7)$$

$$Q_{\pm 1}^{(1)} = -\frac{1}{2} [Q_{xz} - Q_{zx} \pm i (Q_{zy} - Q_{yz})] \quad (8)$$

$$Q_0^{(2)} = \frac{1}{\sqrt{6}} (2Q_{zz} - Q_{xx} - Q_{yy}) \quad (9)$$

$$Q_{\pm 1}^{(2)} = \frac{1}{2} [\mp (Q_{xz} + Q_{zx}) - i (Q_{yz} + Q_{zy})] \quad (10)$$

$$Q_{\pm 2}^{(2)} = \frac{1}{2} [(Q_{xx} - Q_{yy}) \pm i (Q_{xy} + Q_{yx})] \quad (11)$$

and transform under rotation between the two frames as follows:³⁹

$$Q_m^{(k)} = \sum_{m'} (-1)^{m-m'} Q_{m'}^{(k)} D_{-m, -m'}^{(k)}, \quad (12)$$

where $D_{-m, -m'}^{(k)}$ are the Wigner D -matrices. The traceless definition of the components $Q_{\alpha\beta}$ (Eq. (5)) and the property of being symmetric under interchange of the indices α, β implies that $Q_0^{(0)} = Q_m^{(1)} = 0$, such that only the second rank components of the quadrupole moment are non-zero. This allows one to write the transition linestrength using the DUO eigenfunctions (Eq. (2)) as

$$S_{fi} = g_{\text{ns}} \sum_{M_i, M_f} \sum_{m=-2}^2 |\langle \psi_{J_f M_f \tau_f} | Q_m^{(2)} | \psi_{J_i M_i \tau_i} \rangle|^2, \quad (13)$$

where g_{ns} is a nuclear statistical weight that accounts for the degenerate nuclear spin components of the total nuclear-rovibronic wavefunction, see e.g. Bunker and Jensen⁴⁴.

Long⁴³ provides expressions that allows one to construct laboratory frame matrix element expressions for the electric polarisability tensor - also of rank two. Adapting the treatment, one can write the transition quadrupole moment matrix elements as:

$$S_{fi} = g_{\text{ns}} (2J_i + 1)(2J_f + 1) \left| \sum_{\varphi_f} C_{J_i \tau_i}^* (\varphi_f) \sum_{\varphi_i} C_{J_f \tau_f} (\varphi_i) \sum_{m'} \delta_{S_f S_i} \delta_{\Sigma_f \Sigma_i} \times \right. \\ \left. (-1)^{m'+\Omega_i} \langle v_f | \langle \xi_f \Lambda_f | Q_{m'}^{(2)} | \xi_i \Lambda_i \rangle | v_i \rangle \begin{pmatrix} J_i & J_f & 2 \\ -\Omega_i & \Omega_f & -m' \end{pmatrix} \right|^2, \quad (14)$$

where Eq. (12) was used to transform from the laboratory frame to the molecular frame. Here, m and m' index components of the irreducible representation in the laboratory and molecular reference frames, respectively, and the following properties of the Wigner D -matrices, $D_{-m,-m'}^{(k)}$, have been used to express rotational matrix element in terms of the 3- j symbols³⁹

$$|JM\Omega\rangle = (-1)^{M-\Omega} \left(\frac{2J+1}{8\pi^2} \right)^{\frac{1}{2}} D_{-M,-\Omega}^{(J)}, \quad (15)$$

$$\langle JM\Omega| = \left(\frac{2J+1}{8\pi^2} \right)^{\frac{1}{2}} D_{M,\Omega}^{(J)}, \quad (16)$$

$$\int D_{cc'}^C D_{aa'}^A D_{bb'}^B \sin\beta \, d\beta \, d\alpha \, d\gamma = 8\pi^2 \begin{pmatrix} A & B & C \\ a & b & c \end{pmatrix} \begin{pmatrix} A & B & C \\ a' & b' & c' \end{pmatrix} \quad (17)$$

with α , β , and γ the Euler angles. Additionally, the following standard property of the 3- j symbols implies the 3- j symbols containing M_I , M_F and m , which arise as a result of Eq. (17), can be summed over M_f , M_i and m and eliminated from Eq. (13)

$$\sum_{m=-k}^k \sum_{M'=-J'}^{J'} \sum_{M''=-J''}^{J''} \begin{pmatrix} J'' & k & J' \\ M'' & m & -M' \end{pmatrix}^2 = 1. \quad (18)$$

If required, e.g for use with molecular dynamics programs such as RICHMOL,⁴⁵ Duo can explicitly calculate the laboratory frame components of the matrix elements. Note also that the 3- j symbols are invariant under cyclic permutations of their columns and have the properties $|A - B| \leq C \leq |A + B|$, and $a + b + c = 0$. Together with the Kronecker deltas in Eq. (14) this implies following selection rules for E2 transitions:

$$\Delta J = J_f - J_i = 0, \pm 1, \pm 2 \quad (19)$$

and $\Delta S = \Delta \Sigma = 0$, such that

$$\Delta \Lambda = \Lambda_f - \Lambda_i = -m = 0, \pm 1, \pm 2 \quad (20)$$

for all $\langle \xi_f \Lambda_f | Q_m^{(2)} | \xi_i \Lambda_i \rangle$ with $-2 \leq m \leq 2$ in Eq. (14). These quantum number selection rules should be supplemented by the symmetry selection rules:

$$+ \leftrightarrow +, \quad - \leftrightarrow - \quad (21)$$

$$g \leftrightarrow g, \quad u \leftrightarrow u, \quad (22)$$

which arise as a result of the symmetric property of the quadrupole moment under coordinate inversion (Eq. (5)), and the requirement that the total matrix element is also symmetric under coordinate inversion, such that the integral over spatial coordinates is non-zero.

3. Representation of *Ab initio* Coupling Curves

In this section we outline the procedure used by the DUO program to transform coupling curves, specifically including the independent components of the quadrupole moment tensor, from the Cartesian representation commonly obtained from electronic structure calculations, to the tensorial, Λ -representation required by DUO. The (transition) quadrupole moments in Eq. (14) are r -dependent curves (r is the vibrational coordinate) averaged over electronic coordinates:

$$Q_m^{(2)}(r; \xi_f, \xi_i) = \langle \xi_f \Lambda_f | Q_m^{(2)}(r) | \xi_i \Lambda_i \rangle, \quad (23)$$

where $|\xi_i \Lambda_i\rangle$ and $|\xi_f \Lambda_f\rangle$ are the corresponding electronic wavefunctions. These curves are often obtained empirically by fitting analytical functions to experimental measurements of energies and linestrengths, or computed *ab initio* using electronic structure programs such as those used in the present work (MOLPRO^{41,46} or the open-access software CFOUR⁴⁷). In electronic structure calculations the representations of the infinite symmetry groups for diatomic molecules $C_{\infty v}$ and $D_{\infty h}$ are commonly represented in terms of their Abelian subgroups C_{2v} and D_{2h} in order to facilitate the computation of physically-realised energy levels. For the practical purpose of transforming the electronic properties from the output of quantum chemistry programs to the representation required for the DUO input, we also employ the representation of $C_{\infty v}$ and $D_{\infty h}$ in terms of the Abelian subgroups in the following derivation.

The irreducible Abelian representation of a matrix element of a given operator coupling electronic states i and f , each with irreducible Abelian representations G_i and G_f respectively, must be contained within the Abelian group given by the direct product $G_i \times G_f$.²³ Moreover, it can be shown that there exists only one independent Cartesian quadrupole component that couples a given pair of irreducible representations within an Abelian symmetry group. Tables III and IV establish correlations between the products of Cartesian vectors r_x, r_y, r_z , corresponding to components of the quadrupole moment operator in Eq. (5), and the products of different irreducible representations, for C_{2v} and D_{2h} point groups, respec-

TABLE I. Irreducible representations for homonuclear symmetry groups, and corresponding components of electronic states. Appendix A gives the same table with addition of the MOLPRO enumerations.

Symmetry	Components
A_g	$\Sigma_g^+, (\Delta_g)_{xx}$
B_{1g}	$\Sigma_g^-, (\Delta_g)_{xy}$
B_{2g}	$(\Pi_g)_x$
B_{3g}	$(\Pi_g)_y$
A_u	$\Sigma_u^-, (\Delta_u)_{xy}$
B_{1u}	$\Sigma_u^+, (\Delta_u)_{xx}$
B_{2u}	$(\Pi_u)_y$
B_{3u}	$(\Pi_u)_x$

TABLE II. Irreducible representations for heteronuclear symmetry groups, and corresponding components of electronic states. Appendix A gives the same table with addition of the MOLPRO enumerations.

Symmetry	Components
A_1	Σ^+, Δ_{xx}
A_2	Σ^-, Δ_{xy}
B_1	Π_x
B_2	Π_y

tively.

Eq. (14) uses a tensorial representation of all electronic properties, including the electric quadrupole moments $Q_m^{(2)}(r)$. It is also convenient to represent the electronic basis functions $|\xi\Lambda\rangle$ corresponding to doubly degenerate $\Lambda > 0$ states in the tensorial representation with $\pm|\Lambda|$ as a good quantum number. These are related to the Cartesian components $|\alpha\rangle$ and $|\beta\rangle$ by³⁸

$$|\xi, \pm|\Lambda\rangle = \frac{1}{\sqrt{2}} [|\alpha\rangle \pm i|\beta\rangle], \quad (24)$$

where $|\alpha\rangle$ and $|\beta\rangle$ are, for example, $|\Pi_x\rangle$ and $|\Pi_y\rangle$ ($|\Lambda| = 1$), $|\Delta_{xx}\rangle$ and $|\Delta_{xy}\rangle$ ($|\Lambda| = 2$) etc. as typically produced by electronic structure methods.

TABLE III. Product table for the quadratic functions of Cartesian components and the isotropic function s , that transform as the product of different irreducible representations for the C_{2v} point group.

	A_1	A_2	B_1	B_2
A_1	s	xy	xz	yz
A_2	xy	s	yz	xz
B_1	xz	yz	s	xy
B_2	yz	xz	xy	s

We now consider the unitary transformation from the Cartesian (‘electronic structure’) representation of the matrix elements $\langle \xi''\gamma'' | Q_{ij}(r) | \xi'\gamma' \rangle$ ($\gamma \in [\alpha, \beta]$) to their tensorial (‘DUO’) representation $\langle \xi''\Lambda'' | Q_m^{(k)}(r) | \xi'\Lambda' \rangle$ in Eq. (23).

To construct this transformation and also to keep track of the relative phases of ‘electronic structure’ wavefunctions DUO makes the use of the Cartesian matrix elements of the electronic angular momentum operator \hat{L}_z . We choose the Cartesian components $|\alpha\rangle, |\beta\rangle$ such that for wavefunctions with $|\Lambda| > 0$ the \hat{L}_z matrix is given (up to an arbitrary phase factor) by:

$$\mathbf{L}_z = \begin{pmatrix} \langle \alpha | \hat{L}_z | \alpha \rangle & \langle \alpha | \hat{L}_z | \beta \rangle \\ \langle \beta | \hat{L}_z | \alpha \rangle & \langle \beta | \hat{L}_z | \beta \rangle \end{pmatrix} = \begin{pmatrix} 0 & -i\hbar|\Lambda| \\ i\hbar|\Lambda| & 0 \end{pmatrix}, \quad (25)$$

where \mathbf{L}_z is the Cartesian matrix representation of \hat{L}_z with the elements $\langle \xi\gamma'' | L_z | \xi\gamma' \rangle$ and the index ξ is dropped for simplicity. The wavefunctions $|\xi, \pm|\Lambda|\rangle$ in Eq. (24) can be formed as eigenfunctions of the operator \hat{L}_z in the Cartesian representation by diagonalizing the 2×2 matrix \mathbf{L}_z with the eigenvalues $\hbar|\Lambda|$ and $-\hbar|\Lambda|$.³⁸ The corresponding unitary matrix that diagonalizes \mathbf{L}_z ,

$$U = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{-i}{\sqrt{2}} \end{pmatrix} \quad (26)$$

provides the transformation between the Cartesian and tensorial representations for any electronic structure property, including the electric quadrupole

$$Q^{\text{tens.}} = U^{-1} Q^{\text{Cart.}} U. \quad (27)$$

Together with the 3- j symbol in Eq. (14), which implies that each component $Q_{m'}^{(2)}$ couples electronic states with $\Lambda_f - \Lambda_i = m'$, this allows for the following additional relations to be

TABLE IV. Product table for the quadratic functions of Cartesian components and the isotropic function s , that transform as the product of different irreducible representations for the D_{2h} point group.

	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
A_g	s	xy	xz	yz				
B_{1g}	xy	s	yz	xz				
B_{2g}	xz	yz	s	xy				
B_{3g}	yz	xz	xy	s				
A_u					s	xy	xz	yz
B_{1u}					xy	s	yz	xz
B_{2u}					xz	yz	s	xy
B_{3u}					yz	xz	xy	s

made

$$\begin{aligned} \langle \pm|\Lambda||Q_0^{(2)}|\pm|\Lambda\rangle &= \frac{3}{2\sqrt{6}} \left[\langle \alpha|Q_{zz}|\alpha\rangle + \langle \beta|Q_{zz}|\beta\rangle \right] \\ &= \frac{3}{\sqrt{6}} \langle \alpha|Q_{zz}|\alpha\rangle, \end{aligned} \quad (28)$$

$$\begin{aligned} \langle \Sigma^+|Q_{\pm 1}^{(2)}|\mp\Pi\rangle &= \mp\frac{1}{\sqrt{2}} \left[\langle \Sigma^+|Q_{xz}|\Pi_x\rangle + \langle \Sigma^+|Q_{yz}|\Pi_y\rangle \right] \\ &= \mp\sqrt{2} \langle \Sigma^+|Q_{xz}|\Pi_x\rangle, \end{aligned} \quad (29)$$

$$\begin{aligned} \langle \Sigma^-|Q_{\pm 1}^{(2)}|\mp\Pi\rangle &= -\frac{i}{\sqrt{2}} \left[\langle \Sigma^-|Q_{xz}|\Pi_y\rangle + \langle \Sigma^-|Q_{yz}|\Pi_x\rangle \right] \\ &= -i\sqrt{2} \langle \Sigma^-|Q_{xz}|\Pi_y\rangle, \end{aligned} \quad (30)$$

$$\begin{aligned} \langle \Sigma^+|Q_{\pm 2}^{(2)}|\mp\Delta\rangle &= +\frac{1}{\sqrt{2}} \left[\langle \Sigma^+|Q_{xx}|\Delta_{xx}\rangle + \langle \Sigma^+|Q_{xy}|\Delta_{xy}\rangle \right] \\ &= +\sqrt{2} \langle \Sigma^+|Q_{xx}|\Delta_{xx}\rangle, \end{aligned} \quad (31)$$

$$\begin{aligned} \langle \Sigma^-|Q_{\pm 2}^{(2)}|\mp\Delta\rangle &= \pm\frac{i}{\sqrt{2}} \left[\langle \Sigma^-|Q_{xx}|\Delta_{xy}\rangle + \langle \Sigma^-|Q_{xy}|\Delta_{xx}\rangle \right] \\ &= \pm i\sqrt{2} \langle \Sigma^-|Q_{xx}|\Delta_{xy}\rangle, \end{aligned} \quad (32)$$

$$\begin{aligned} \langle \mp\Pi|Q_{\pm 1}^{(2)}|\mp\Delta\rangle &= \mp\frac{1}{2} \left[\langle \Pi_x|Q_{xz}|\Delta_{xx}\rangle + \langle \Pi_x|Q_{yz}|\Delta_{xy}\rangle - \langle \Pi_y|Q_{yz}|\Delta_{xx}\rangle + \langle \Pi_y|Q_{xz}|\Delta_{xy}\rangle \right] \\ &= \mp 2 \langle \Pi_x|Q_{xz}|\Delta_{xx}\rangle, \end{aligned} \quad (33)$$

The initial expressions in Eqs. (28-33) are obtained from Eqs. (9-11) by substituting the symmetric components $Q_{zx} = Q_{xz}$, $Q_{zy} = Q_{yz}$, $Q_{xy} = Q_{yx}$, and $Q_{xx} = -Q_{yy}$. The second line in each expression is obtained by setting matrix elements that do not satisfy the selection rule in Eq. (20) (e.g. $\langle \Sigma^+ | Q_{\mp 1}^{(2)} | \mp \Pi \rangle$, $\langle \Sigma^+ | Q_{\mp 2}^{(2)} | \mp \Delta \rangle$, etc.) equal to zero and rearranging to obtain relations between different Cartesian components of the matrix elements. In the case of D_{2h} symmetry, the corresponding equations (28-33) are identical except for the addition of the relevant g/u parity label.

III. DEMONSTRATIONS

In this section we provide a demonstration of the DUO electric quadrupole program for the simple $^1\Sigma$ systems of H_2 , CO and HF. In particular, we choose H_2 as the initial proof of the program due to the highly accurate spectroscopic data available for this molecule, which we aim to reproduce. The demonstrations for CO and HF exemplify heteronuclear systems with large molecular quadrupole moments in which the consideration of E2 transitions is necessary to obtain accurate cross-sections. An application to an more complex system involving interstate transitions with a non- Σ electronic state is illustrated by way of simulating the Noxon electronic (E2) band $a^1\Delta_g - b^1\Sigma_g^+$ of the O_2 molecule. The spectroscopic models detailed in this section are provided as supplementaries in the form of DUO input files, the DUO program itself is open-source and can be obtained from the ExoMol public repository at github.com/Exomol.

A. Molecular Hydrogen

Molecular hydrogen is the simplest diatomic molecule, containing just two electrons and two protons. It is the most abundant molecule in the universe and plays an important role in star formation,⁴⁸⁻⁵¹ interstellar physics,⁵²⁻⁵⁴ (exo)planetary atmospheres,⁵⁵⁻⁵⁸ and investigations of fundamental physics.^{59,60}

Owing to its molecular symmetry, the homonuclear H_2 molecule has no permanent electric dipole moment, and thus rovibrational transitions are forbidden in the electric dipole approximation. The availability of highly accurate electronic potential energy curves (PECs) and electric quadrupole moment curves (QMCs) makes H_2 an ideal candidate for validating

the implementation of E2 transitions in DUO. The simplicity of the H₂ molecule makes it an extremely tractable quantum mechanical problem - indeed, it was the model molecule for many early calculations of molecular dynamics, on the world's first mass-produced computers.⁶¹⁻⁶³ Even for these early calculations linestrength accuracies within a few percent were attainable.⁶⁴⁻⁶⁶ As a result, there is a wealth of accurate spectroscopic data available with which the DUO implementation can be validated. Most recently, Roueff *et al.*¹² calculated a highly accurate (order 10⁻⁶ cm⁻¹) infrared spectrum for the H₂ molecule including several higher order correction terms.⁶⁷

The calculations of Roueff *et al.*¹² are based on an extensive series of earlier works by Pachucki⁶⁸, Pachucki and Komasa^{69,70,71}, in which the H₂ Born-Oppernheimer PEC was obtained with 10⁻¹⁵ relative numerical precision using 22,000 exponential basis functions and explicit electron correlation calculations.^{68,72} They also compute non-adiabatic,^{69,71} adiabatic⁷⁰ and high-order relativistic⁷³ corrections to the Born-Oppenheimer potential energy. The quadrupole moment function employed in their calculations is obtained using the Born-Oppenheimer wavefunction, and is in agreement with the values reported by Wolniewicz, Simbotin, and Dalgarno¹⁰, who employ a 494-term correlated basis representation of the wavefunction to obtain the quadrupole moment function with an estimated accuracy on the order of 0.001%.

For the validation of the DUO implementation, their original Born-Oppenheimer potential is retrieved using the V(DR) function made available via the H2SPECTRE program.⁶⁷ The contribution of the adiabatic and non-adiabatic corrections computed by Roueff *et al.*¹² are in the range 5–20 cm⁻¹ and 0.4–4.0 cm⁻¹, respectively, increasing the total state energy. The higher order relativistic corrections are on the order of 0.01 cm⁻¹ or less. Since the Born-Oppenheimer PEC provided does not include adiabatic or non-adiabatic corrections, significant deviation is expected between the calculated state energies for high v and J states. Typically these deviations could be corrected in DUO via an empirical fit to experimentally accurate state energies. Such refinement is not performed in this work, as the aim here is to illustrate the implementation of E2 transition strengths, rather than provide an accurate or improved line list for H₂. The quadrupole moment function of Wolniewicz, Simbotin, and Dalgarno¹⁰ is also employed, given as a grid of 253 E2 moment values between 0.2–20.0 a_0 , which DUO interpolates using quintic splines.

The vibrational grid is defined by 501 equally spaced points in the range 0.38–18.90 a_0 .

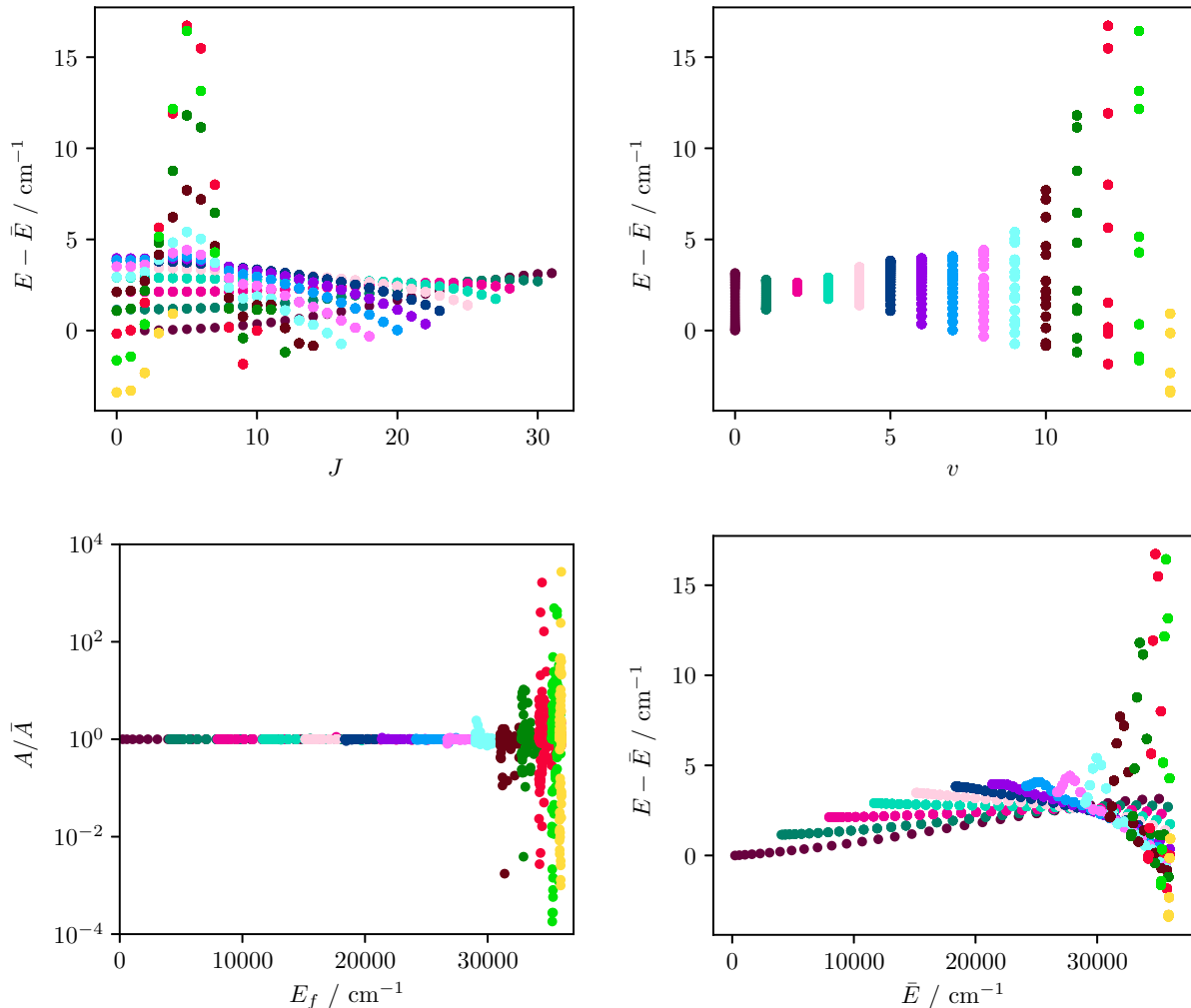


FIG. 1. Agreement between the Einstein-A coefficients (bottom-left) and state energies of H_2 calculated by DUO (A_{if}, E), and by Roueff *et al.*¹² ($\bar{A}_{\text{if}}, \bar{E}$). The energy differences $E - \bar{E}$ in the upper panels are plotted as functions of the level of rotational J and vibrational v excitations. The energy and A -coefficient differences in the lower panels are plotted as functions of (upper) state energy. The colors in each plot correspond to the (upper) vibrational quantum number of the state.

After solving the vibrational Schrödinger using the sinc-DVR method, the first 30 vibrational states are selected to form the contracted vibrational basis and the rovibrational Schrödinger equation is solved for rotational states with total angular momentum quantum numbers $0 \leq J \leq 200$ at 296 K.

Fig. 1 illustrates the results of a line-by-line comparison of the DUO results to the

accurate line list of Roueff *et al.*¹² (including all corrections). As expected, significant differences between the energies calculated by DUO (E) and the accurate energies provided by H2SPECTRE (\bar{E}) for high v , J states are observed. We also expect to see significant deviation in the Einstein coefficients obtained for transitions involving these states, due to the factor of ν_{fi}^5 present in Eq. 3 coupled with vanishingly small Einstein coefficients for transitions to states with large v quantum number. Thus states with $v \geq 10$ are excluded from the analysis.

For the 3,027 remaining transitions between the remaining vibrational levels, 99.0% of Einstein coefficients (A_{fi}) lie within 1% of the values calculated by Roueff *et al.*¹² (\bar{A}_{fi}). The 99-th percentile is $|1 - A_{fi}/\bar{A}_{fi}| = 0.0672$. Note that all Einstein coefficients with errors greater than 5% correspond to weak transitions with absorption intensities $I_{fi} < 1 \times 10^{-35}$ cm molecule⁻¹. For example, the largest discrepancy $A_{fi}/\bar{A}_{fi} = 2.45$ corresponds to the $v = 9 \leftarrow 0$ transition with $A_{fi} = 5.27 \times 10^{-15}$ s⁻¹ and $I_{fi} = 5.45 \times 10^{-36}$ cm molecule⁻¹.

Table V compares the results of the calculation to the experimentally measured intensities and line position of Bragg, Brault, and Smith⁷⁴ ($T = 296$ K), and in Table VI to more recent measurements of Campargue *et al.*⁷⁵, as well as their theoretical predictions based on the effective quadrupole moment method. The Duo calculated intensities reproduce closely the accurate experimental measurements of Campargue *et al.*⁷⁵, and match their theoretical predicted values to within 0.1%. Agreement with the older measurements of Bragg, Brault, and Smith⁷⁴ are less consistent but generally agree, particularly for the Q -branch transitions of the first overtone band. In both cases the line positions differ considerably, but by a roughly constant value across each vibrational band. This is due to the fact that no DUO refinement procedure is performed and no adiabatic or non-adiabatic corrections are included in the calculations. Also illustrated, in Fig. 2 are (left) direct comparisons of the Einstein coefficients obtained via DUO to those of Roueff *et al.*¹², and (right) the absorption intensities via the EXOCROSS program, as compared to transitions listed in the HITRAN²⁶ database. Here and in the following we use the HITRAN intensity units cm/molecule.

B. Carbon Monoxide

Carbon monoxide is a heteronuclear diatomic molecule, and thus electric dipole transitions are allowed within its ground $X^1\Sigma^+$ state. However, it also possesses a strong electric

TABLE V. Comparison of various H_2 $v' \leftarrow 0$ transitions (positions and intensities), measured experimentally by Bragg, Brault, and Smith⁷⁴, to the values predicted by DUO calculations at $T = 296$ K. The line positions are in cm^{-1} .

v'	Branch	$\tilde{\nu}_{\text{obs.}} - \tilde{\nu}_{\text{calc.}}^{\text{DUO}}$	$I_{\text{obs.}}/I_{\text{calc.}}^{\text{DUO}}$
1	Q(3)	-1.158	1.080
1	Q(2)	-1.165	1.027
1	Q(1)	-1.171	1.040
1	S(0)	-1.181	1.158
1	S(1)	-1.185	1.648
1	S(2)	-1.185	1.594
1	S(3)	-1.187	1.013
2	O(3)	-2.121	0.852
2	O(2)	-2.138	0.915
2	Q(3)	-2.121	0.949
2	Q(2)	-2.136	0.973
2	Q(1)	-2.147	1.624
2	S(0)	-2.152	0.984
2	S(1)	-2.147	0.988
3	S(0)	-2.923	0.816
3	S(1)	-2.912	0.911
3	S(2)	-2.887	1.017
3	S(3)	-2.858	0.878
4	S(0)	-3.480	0.606
4	S(1)	-3.469	0.874
4	S(2)	-3.432	0.727
4	S(3)	-3.382	0.831

TABLE VI. Comparison of various H_2 $v' = 2 \leftarrow 0$ overtone lines, measured experimentally and computed via an effective quadrupole moment by Campargue *et al.*⁷⁵ ($\tilde{\nu}_{\text{calc.}}$), and the values predicted by DUO calculations ($\tilde{\nu}_{\text{calc.}}^{\text{DUO}}$) for $T = 296$ K. The line positions are in cm^{-1} .

Branch	$\tilde{\nu}_{\text{obs.}} - \tilde{\nu}_{\text{calc.}}$	$I_{\text{obs.}}/I_{\text{calc.}}$	$\tilde{\nu}_{\text{obs.}} - \tilde{\nu}_{\text{calc.}}^{\text{DUO}}$	$I_{\text{obs.}}/I_{\text{calc.}}^{\text{DUO}}$
O(5)	-0.0019	0.924	-2.061	0.924
O(4)	-0.0040	0.931	-2.093	0.930
O(3)	-0.0033	1.008	-2.115	1.007
O(2)	-0.0031	1.001	-2.132	1.000
O(5)	-0.0030	1.020	-2.067	1.020

quadrupole moment,⁷⁷ and as a result, the electric dipole infrared spectrum is accompanied by weaker electric quadrupole lines. We show that many of the E2 spectral lines at room temperature lie higher in intensity than the minimum spectroscopic cutoff of 10^{-30} $\text{cm}^2/\text{molecule}$ at the HITRAN reference temperature of $T = 296$ K, typically applied to E1 spectra. As a result, their inclusion or omission in spectroscopic databases has significant

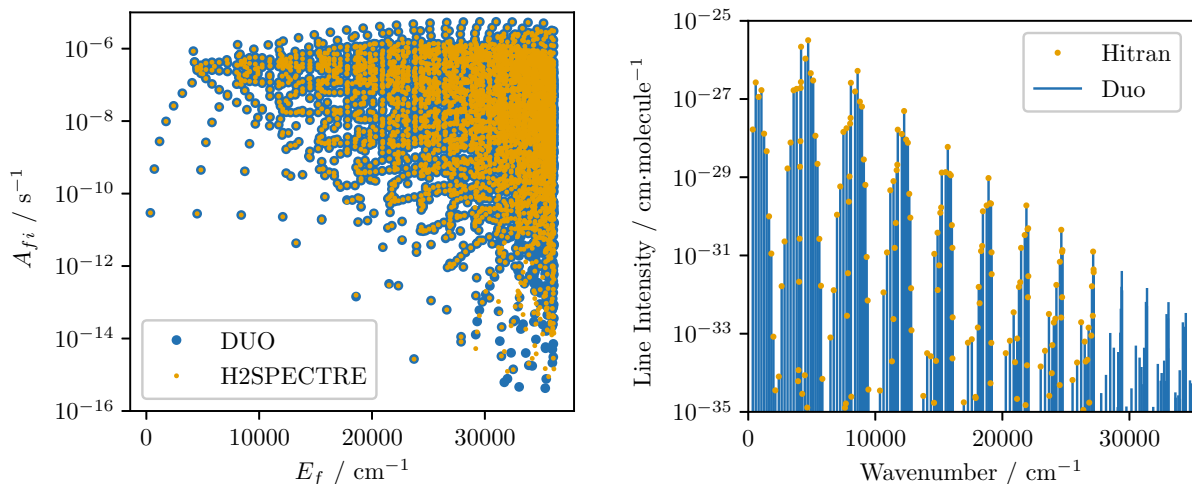


FIG. 2. Comparison of the DUO calculated Einstein- A coefficients with the target values predicted by Roueff *et al.*¹² (left), and of the DUO calculated absorption intensities ($T = 296$ K) with the intensities listed in the HITRAN database^{10,26,76} (right).

implications for applications where accurate cross-sections are required.

Numerous experimental and *ab initio* studies have been performed of the electric dipole moment spectra for the CO molecule, including recent accurate calculations by Li *et al.*⁷⁸. Li *et al.* seek to resolve a long-standing uncertainty in the line intensities of CO E1 spectra, namely significant differences observed between the intensities predicted by the calculations of Goorvitch⁷⁹ and those of Huré and Roueff⁸⁰. The former uses Chackerian’s⁸¹ semi-empirical dipole moment function, obtained from a nonlinear least-squared fit to vibrational states up to $v = 38$. The latter uses a purely *ab initio* electric dipole moment curve (DMC), computed by Langhoff and Bauschlicher via ACPF calculations on a 5Z basis set.⁸² Li *et al.* perform new CRDS measurements in order to produce an accurate DMC via a direct-fit. At long bond lengths, where experimental data is not attainable, they reproduce the calculations of Langhoff and Bauschlicher⁸² but with a finer grid, and determine that the interpolation used on the original grid was insufficient to capture the full shape of the DMC. Their PEC of choice is the analytical MLR3 function obtained by Coxon and Hajigeorgiou⁸³ via a direct fit to 21559 spectroscopic lines.⁸³

Studies of the quadrupole moment of CO are somewhat sparser. Although several experimental measurements exist for the equilibrium molecular quadrupole moment, only a single study presents a QMC across a range of geometries. The early work by Truhlar⁴² presents

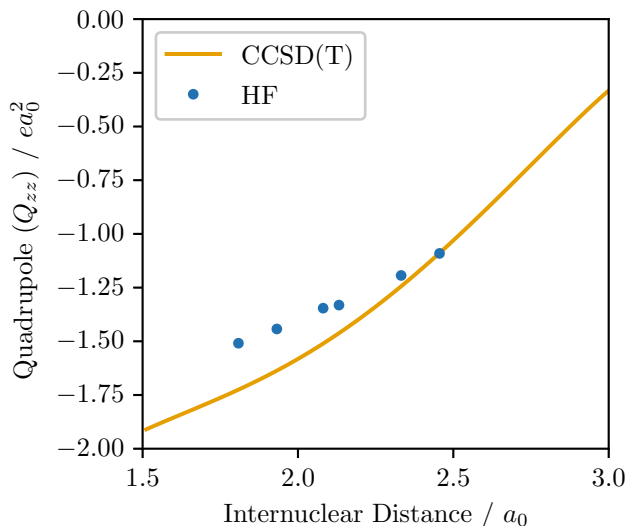


FIG. 3. Electric quadrupole moments in a.u. (ea_0^2) for CO obtained in this work via CCSD(T) calculations compared to Hartree-Fock calculations by Truhlar⁴².

simple Hartree-Fock calculations of the quadrupole moment at just 6 internuclear geometries. The accuracy of the vibrational matrix elements calculated is low, particularly for weaker transitions corresponding to higher vibrational quantum numbers. In particular the methodology struggles to accurately describe the quadrupole moment at intermediate and long internuclear distances, which are necessary for calculating the vibrational overtones. Coriani *et al.*⁸⁴ compares the results of CCSD and CC3 calculations on the CO molecule with a variety of basis sets. The results show that the CCSD level of theory is insufficient to correctly describe the electric properties of the CO molecule, and that consideration of triple excitations is vital. They also study the convergence of such calculations with increasing basis set size, and find the results converge quickly for bases larger than DZ.

In the present work, following the success of Coriani *et al.*⁸⁴, the CCSD(T) method is employed with an aug-cc-pwCVQZ basis as implemented in the CFOUR program⁴⁷ to calculate the strength of the non-zero quadrupole component Q_{zz} for 100 nuclear geometries in the range 1.50–3.78 a_0 . Divergent behaviour at large internuclear separations is attributed to CCSD(T)'s inability to account for multireference effects. The curve is therefore truncated at 3.0 a_0 . The QMC obtained from these calculations is shown in Fig. 3.

The value of the electric quadrupole moment curve at equilibrium separation $Q_{zz} = -1.45$ a.u. (a.u. = ea_0^2) agrees reasonably well with the Hartree-Fock calculations of Truh-

TABLE VII. A comparison of various electric quadrupole moment values for CO in a.u. ($ea_0^2 = 4.486\,484(28) \times 10^{-40} \text{ C m}^2$ ⁸⁶) from the literature. All values are averaged over the vibrational ZPE and are given in the molecular centre of mass reference frame, $Q_{zz}^{(\text{CM})} = 2R_z\mu + Q_{zz}^{(\text{EQC})}$ with the displacement between the centre of mass and the electric quadrupole centre given by $R_z = -5.96$ a.u. and a dipole moment $\mu = -0.043\,159$ a.u.^{77,84}

Q_{zz} / a.u.	Method	Ref.
-1.4522	CCSD(T)	This work
-1.445(2)	CC3	84
-1.43(3)	MBERS	85
-1.440(69)	EFGIB	77
-1.382(31)	EFGIB	77 and 87
-1.18(22)	EFGIB	77 and 88

lar⁴², which obtain $Q_{zz} = -1.33$ a.u.. Note that Truhlar⁴² chooses a definition of the quadrupole moment which is a factor of two larger than the definition employed by MOLPRO and DUO, the value quoted here is adjusted accordingly. Importantly, we obtain very good agreement with experimental values of the ZPE-averaged quadrupole moment from the literature. From the CCSD(T) quadrupole moment shown in Fig. 3, DUO calculates $\langle v=0 | Q_{zz} | v=0 \rangle = -1.4522$ a.u. which agrees closely with the accurate MBERS measurement of Meerts, Leeuw, and Dymanus⁸⁵, the CC3 calculations of Coriani *et al.*⁸⁴, and EFGIB measurements from other sources. These comparisons are presented in Table VII.

Nuclear motion calculations are performed using the semi-empirical PEC of Meshkov *et al.*⁸⁹. This accurate analytical representation of the PEC is chosen for the DUO solutions in order to improve the quality of the wavefunctions used to calculate the linestrengths. The DUO vibrational grid used for the calculation consists of 501 equally spaced points in the range 1.50–3.00 a_0 , and the first 21 vibrational states are selected to form the contracted basis. These excitations correspond to energies within the spectroscopically relevant region ($E/hc < 40.000 \text{ cm}^{-1}$) for the room temperature applications.

After solving the Schrödinger equation for rotational quantum numbers $0 \leq J \leq 50$, with

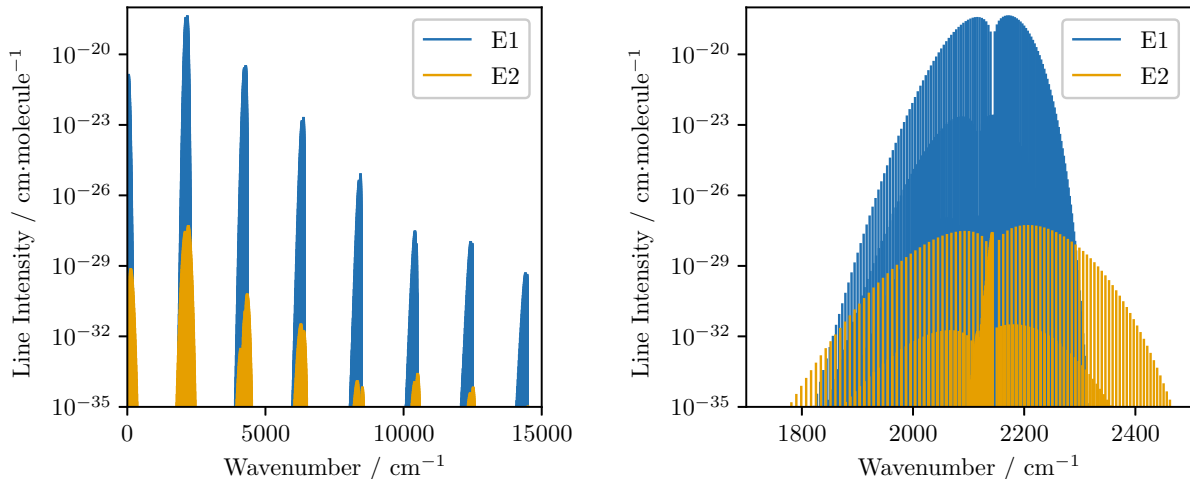


FIG. 4. Vibrational bands (left) and rotational $v = 0 - 1$ transitions (right) of the E1 and E2 rovibrational spectra in the ground $X \ ^1\Sigma^+$ state of the $^{12}\text{C}^{16}\text{O}$ molecule. The E1 intensities are those of Li *et al.*⁷⁸, via the ExoMol database.

a vibrational transition quadrupole moment $\langle \xi_f v_f | Q_0^{(2)} | \xi_i v_i \rangle < 1 \times 10^{-5}$ a.u. are discarded. It was found by Medvedev *et al.*⁹⁰ numerically computed transition dipole moments of high overtones corresponding to large changes in vibrational quanta can suffer from numerical instabilities and lead to unphysically large intensities. In the case of electric quadrupole transitions however, the intensity of these high overtone vibrational bands is sufficiently weak that absorption lines with transition quadrupole moments $\langle \xi_f v_f | Q_0^{(2)} | \xi_i v_i \rangle < 1 \times 10^{-5}$ a.u. (corresponding to high overtone bands) can simply be excluded from the line list altogether.

The calculated state energies are substituted for those obtained by Li *et al.*⁷⁸ in a simultaneous direct-fit to experimentally determined energy levels. This improves the accuracy in the line positions of the final stick spectrum, obtained via EXOCROSS⁹¹, but has no effect on the quadrupole Einstein coefficients or linestrengths. The energy level data of Li *et al.*⁷⁸ is made available through the HITRAN or ExoMol (exomol.com) databases.³¹

The resultant room temperature ($T = 296$ K) line list for $^{12}\text{C}^{16}\text{O}$ with a cut-off intensity of 10^{-35} cm molecule⁻¹ consists of 6474 electric quadrupole transitions between rotational states up to $J_{\text{max}} = 48$, and vibrational states $v = 7$. A synthetic room temperature E2 spectrum is illustrated in Fig. 4, where it is compared to the E1 spectrum of Li *et al.*⁷⁸. The difference is approximately eight orders of magnitude. Nonetheless, many E2 lines -

f	i	A_{fi}	$\tilde{\nu}_{fi}$
94	10	1.0587E-17	10.591935
93	9	1.1546E-17	10.696876
92	8	1.2569E-17	10.801832
91	7	1.3657E-17	10.906802
90	6	1.4815E-17	11.011786
89	5	1.6043E-17	11.116781
88	4	1.7346E-17	11.221787
87	3	1.8725E-17	11.326802
86	2	2.0183E-17	11.431825
85	1	2.1722E-17	11.536856
136	52	1.7502E-16	17.652735

TABLE VIII. Extract from the $^{12}\text{C}^{16}\text{O}$ electric quadrupole Transition file. It contains the upper (f) and lower (i) states counting numbers, Einstein A coefficients (s^{-1}) and transition wavenumbers (cm^{-1}).

particularly for the $v = 0 \leftarrow 0$ and $v = 1 \leftarrow 0$ bands - lie above the typical cutoff intensity used in many spectroscopic databases ($\sim 10^{-30} \text{ cm}^2 \text{ molecule}^{-1}$ at $T = 296 \text{ K}$).

The computed electric quadrupole Einstein A coefficients of $^{12}\text{C}^{16}\text{O}$ are combined with the ExoMol E1 line list Li2015 for CO in a form of an E2 Transition file, see an extract in Table VIII. Apart from the Einstein A E2 coefficients (s^{-1}), the Transition file contains the upper and lower state counting numbers of the Li2015 State file, as illustrated in Table IX, which presents an extract from the ExoMol State file of the $^{12}\text{C}^{16}\text{O}$ line list Li2015. For more details on the ExoMol line list structure see Tennyson *et al.*³¹.

C. Hydrogen Fluoride

Like the CO molecule, HF possesses a strong permanent electric dipole moment⁹³, it also possesses a strong permanent electric quadrupole moment.⁹⁴ Numerous *ab initio* studies have been performed for HF, including several which produce QMCs for the ground $X^1\Sigma^+$ electronic state.⁹⁵⁻⁹⁷ Piecuch *et al.*⁹⁵ use the orthogonally spin-adapted linear-response

TABLE IX. Extract from the Li2015 States file for $^{12}\text{C}^{16}\text{O}$.

i	E	g	J	v	τ
1	0.000000	1	0	0	e
2	2143.271100	1	0	1	e
3	4260.062200	1	0	2	e
4	6350.439100	1	0	3	e
5	8414.469300	1	0	4	e
6	10452.222200	1	0	5	e
7	12463.768600	1	0	6	e
8	14449.181300	1	0	7	e
9	16408.534600	1	0	8	e
10	18341.904400	1	0	9	e
11	20249.368200	1	0	10	e

i : State counting number.

\tilde{E} : State energy in cm^{-1} .

g_i : Total statistical weight, equal to $g_{\text{ns}}(2J + 1)$.

J : Total angular momentum.

State: Electronic state.

v : State vibrational quantum number.

τ : Rotationless parity e/f .⁹²

coupled-cluster (LRCC) theory with singly and doubly excited clusters (CCSD) and obtain quadrupole moments at 15 internuclear geometries in the range 1.126 32–12.1296 a_0 . Their basis set of choice is that introduced by Sadlej for correlated calculations of molecular electric properties,⁹⁸ which they compare to standard basis sets at the TZ level. They also provide the results of full CI calculations on a DZ basis set. Maroulis⁹⁶ presents all-electron CCSD(T) calculations of the quadrupole moment at nine internuclear geometries in the range 0.9328–2.5328 a_0 . For comparison, the quadrupole moment for the $X^1\Sigma^+$ state is computed via the MRCI method and an aug-cc-pVQZ basis set at 501 internuclear geometries in the range 1.32–6.99 a_0 using MOLPRO.

The electric quadrupole moments of HF obtained via these various methods are illus-

TABLE X. A comparison of various *ab initio* electric quadrupole moment values for HF in a.u. (ea_0^2). All values are given in the molecular centre of mass reference frame, and at the equilibrium nuclear geometry.

Q_{zz} / a.u.	Method	Ref.
1.706	MRCI	This work
1.72	CCSD	95
1.72	CCSD(T)	96
1.66	CI	95

trated in Fig. 5. Although the four curves have the same general shape, significant variation is apparent between the value of Q_{zz} computed at intermediate bond lengths close to $3.8 a_0$. Here the strength of the quadrupole moment is greatest, and difference of more than 0.5 a.u. is apparent between the full CI and CCSD methods. Table X shows the differences in the value of the quadrupole moment at the equilibrium internuclear distance for the four *ab initio* methods presented. All four calculations produce similar values for $Q_{zz}(R_e)$, but the coupled-cluster methods systematically overestimate the strength relative to experimental measurements. Importantly, when averaged over the vibrational ZPE, the MRCI results obtained in the present work give good agreement with the experimental MBERS measurement of de Leeuw and Dymanus⁹⁴. They obtain $\langle v=0|Q_{zz}(r)|v=0\rangle = 1.75(2)$ a.u., whilst DUO calculates a value of 1.747 a.u., which is within the range of experimental uncertainty.

For the PEC, Coxon and Hajigeorgiou⁹⁹ provide a very accurate RKR-style analytical expression for the potential energy and Born-Oppenheimer breakdown functions of the $X^1\Sigma^+$ ground electronic state of various hydrogen halide isotopologues, including $^1\text{H}^{19}\text{F}$. They devise a novel analytical form (MLR3) of the diatomic electronic potential and perform a non-linear least squares fit to experimental energies.

Their analytical representation of the MLR3 potential has been newly implemented in DUO and for the present calculations, the HF MLR3 parameters obtained by Coxon and Hajigeorgiou⁹⁹ are employed, as well as their Born-Oppenheimer breakdown (BOB) function which is obtained from the Fortran source code provided in the supplementary material of Coxon and Hajigeorgiou⁹⁹.

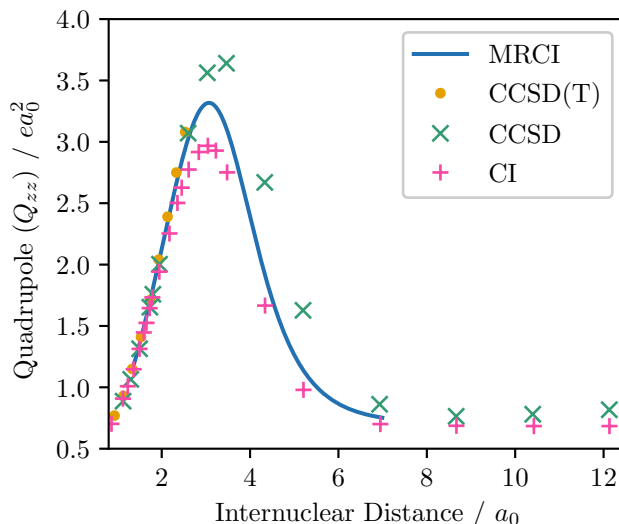


FIG. 5. Comparison of the quadrupole moment curves in a.u. (ea_0^2) for HF obtained via various *ab initio* methods. The MRCI calculations presented in this work, CCSD(T) calculations of Maroulis⁹⁶, and CCSD and full-CI calculations of Piecuch *et al.*⁹⁵.

Fig. 6, shows a comparison of the potential energy curves obtained from our MRCI calculations, the CCSD calculations of Piecuch *et al.*⁹⁵ and the MLR3 potential of Coxon and Hajigeorgiou⁹⁹. All three methods give similar results at short and intermediate bond lengths. The CCSD calculations overestimate the dissociation energy, relative to the empirical MLR3 potential, and the MRCI results predict a slightly lower dissociation energy. Fig. 7 illustrates the results of calculations from two spectroscopic models. In each case the potential energies are the same; the MLR3 and BOB curves of Coxon and Hajigeorgiou⁹⁹; but one model uses the MRCI quadrupole moment presented in this work, and the other uses Piecuch’s CCSD quadrupole moment. In both cases nuclear motion calculations are performed for rotational states $0 \leq J \leq 41$, the vibrational grid is defined for 501 equally spaced points in the range $0.76\text{--}4.40 a_0$, and the first 20 vibrational states are chosen for the contracted basis.

For the first three vibrational bands, the absorption intensities predicted by both spectroscopic models are nearly identical. Higher order vibrational bands, however, exhibit significant discrepancies. The CCSD intensities begin to plateau above $20\,000\text{ cm}^{-1}$, we propose that this intensity plateau arises as a result of the same effect encountered in section III B and detailed by Medvedev *et al.*⁹⁰. Comparatively, the MRCI spectrum shows no such

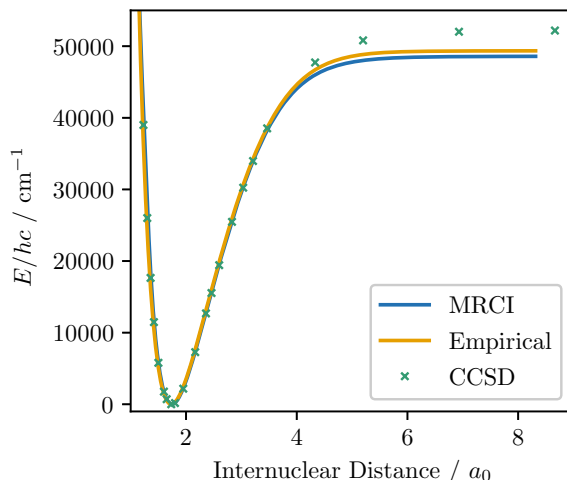


FIG. 6. Comparison of the potential energy curves for the $X^1\Sigma^+$ ground state of HF. The MRCI calculations are from this work, empirically fitted MLR3 potential of Coxon and Hajigeorgiou⁹⁹, and the CCSD calculations of Piecuch *et al.*⁹⁵.

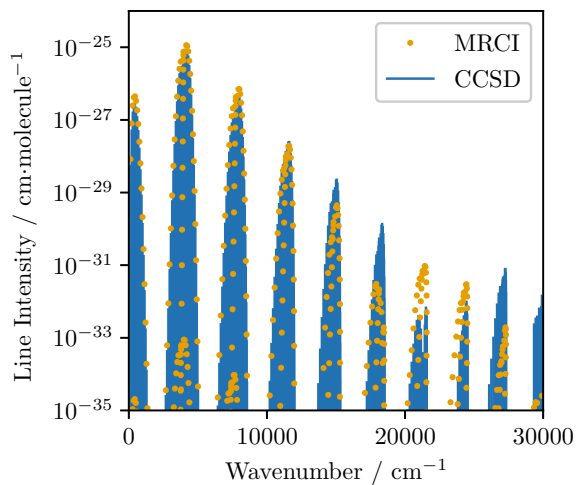


FIG. 7. Comparison of the electric quadrupole absorption spectrum for $H^{19}F$ obtained via spectroscopic models using the CCSD and MRCI quadrupole moment curves illustrated in Fig. 5.

intensity plateau, indeed the MRCI quadrupole moment is obtained on a considerably finer grid spacing, which aids in smoothing the interpolation.

A second possible cause proposed by Medvedev *et al.*⁹⁰ is the asymptotic behaviour of the quadrupole moment curves at longer internuclear distances. Here the magnitude of the coupling becomes exponentially smaller, and significant relative variations in the

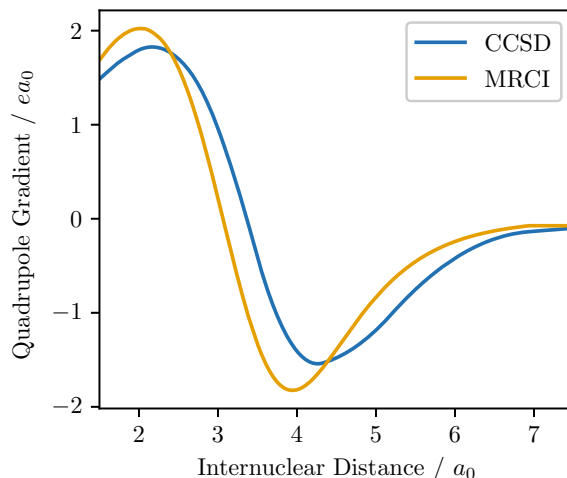


FIG. 8. Central finite difference gradients of the HF quadrupole moment obtained via MRCI and CCSD methods with respect to internuclear distance.

gradient of Q_{zz} are observed between the two methods. The gradient of CCSD quadrupole moment curve at distances $R > 3a_0$ decays considerably slower than that obtained via MRCI calculations. Fig. 8 shows the gradient of the two quadrupole moment functions computed using a central finite difference scheme on the Duo integration grid.

The MRCI spectrum exhibits a local minimum in intensity for the $v = 5 \leftarrow 0$ band. A similar abnormal intensity was observed by Medvedev *et al.*⁹⁰ for the same vibrational band of the electric dipole spectrum. Regardless, the expected E2 absorption intensities for the $v = 5 \leftarrow 0$ band is extremely weak, far weaker than typical spectroscopic cutoff intensity (10^{-30} cm/molecule at $T = 296$ K).

Intensities obtained using the MRCI quadrupole moment are chosen for the final $^1\text{H}^{19}\text{F}$ spectroscopic model and line list. This is combined with the ExoMol E1 line list Coxon-Hajig in the form of an E2 Transition file. Fig. 9 compares the E2 intensities obtained for room temperature calculations to the E1 intensities of Coxon and Hajigeorgiou⁹⁹. It consists of 2716 electric quadrupole transitions between rotational states up to $J = 18$ and vibrational states up to $v = 9$ with a cutoff intensity of 10^{-35} cm molecule⁻¹ ($T = 296$ K) and is included into the supplementary material of this work.

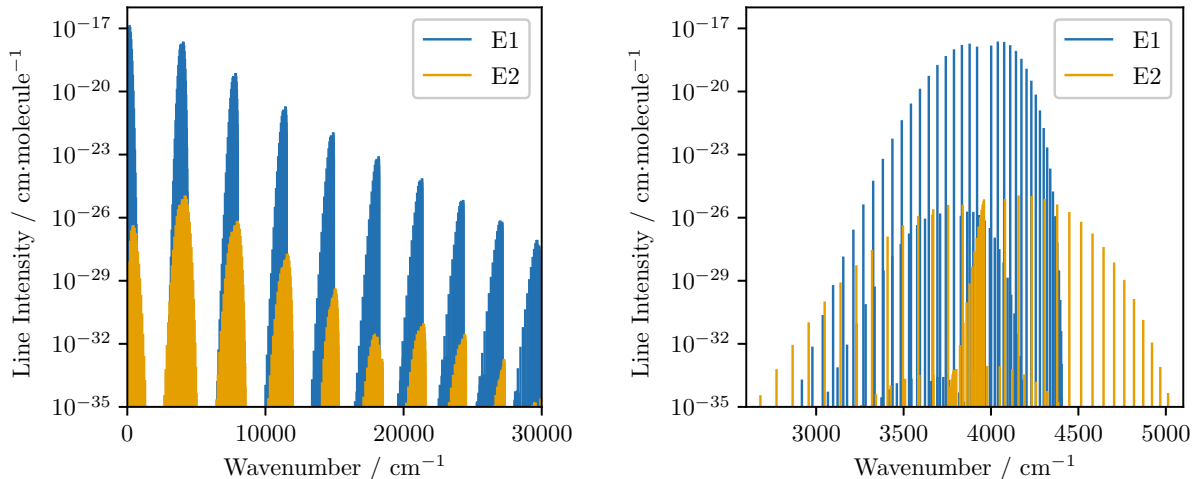


FIG. 9. Vibrational bands (left) and rotational $v = 0 - 1$ transitions (right) of the E1 and E2 rovibrational spectra in the ground $X^1\Sigma^+$ state of the H^{19}F molecule as line intensities ($\text{cm}/\text{molecule}$). The E1 spectrum is that of Coxon and Hajigeorgiou⁹⁹, via the ExoMol database.

D. Oxygen Noxon Band

Owing to its molecular symmetry, the homonuclear O_2 molecule possesses no permanent dipole moment. Additionally, the three lowest lying electronic states, $X^3\Sigma_g^-$, $a^1\Delta_g$ and $b^1\Sigma_g^+$ all have *gerade* symmetry. The Σ spin-orbit mixing results in electric quadrupole transitions in the $a^1\Delta_g - X^3\Sigma_g^-$ system, which borrow strength from the direct $a^1\Delta_g - b^1\Sigma_g^+$ transitions of the so-called Noxon band.^{27,100}

$$\langle a^1\Delta_g | Q_{\pm 2}^{(2)} | X^3\Sigma_g^- \rangle \propto \langle a^1\Delta_g | Q_{\pm 2}^{(2)} | b^1\Sigma_g^+ \rangle \quad (34)$$

Although weak, with intensities on the order of $10^{-45} \text{ cm}^2 \text{ molecule}^{-1}$, rotational lines in both the $(1 - 0)$ and $(0 - 0)$ Noxon bands have been measured experimentally.^{101,102} This electronic band is forbidden by the magnetic dipole $\Delta\Lambda = 0, \pm 1$ selection rule, and consequently the Noxon band is purely quadrupolar in nature. This makes the Noxon band ideal for validations of the electric quadrupole methodology applied to open-shell molecules.

The emission spectrum of the fundamental Noxon band was measured at 313(10) K by Fink *et al.*¹⁰² with an estimated precision of 0.010–0.020 cm^{-1} . This measurement is replicated computationally with DUO calculated Einstein coefficients and the EXOCROSS program. The *ab initio* data for the DUO calculations was produced using MOLPRO¹⁰³ with

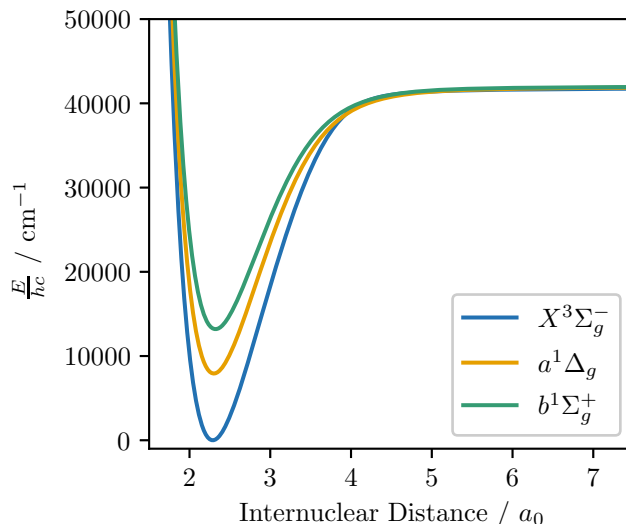


FIG. 10. Potential energy curves for the three lowest lying electronic states of O_2 , obtained via MRCI calculations with an aug-cc-pV6Z basis set.

the MRCI program and an aug-cc-pV6Z basis set. The calculation includes PECs for the three lowest lying electronic states $X^3\Sigma_g^-$, $a^1\Delta_g$ and $b^1\Sigma_g^+$ (Fig. 10), as well as diagonal quadrupole moment curves $Q_0^{(2)}(r) = 3Q_{zz}(r)/\sqrt{6}$ for the $a^1\Delta_g$ and $b^1\Sigma_g^+$ electronic states, and the off-diagonal $a^1\Delta_g - b^1\Sigma_g^+$ quadrupole $Q_{\pm 2}^{(2)}(r) = \sqrt{2}Q_{xx}(r)$ (Fig. 11). Calculations are performed on a grid of 116 internuclear distances in the range 1.5–7.5 a_0 . The contracted vibrational basis set consists of the first 25 vibrational states for each electronic state, and calculations are performed for rotational states $0 \leq J \leq 50$.

Fig. 12 shows an overlay of the experimental spectrum by Fink *et al.*¹⁰² with the calculated emission cross-section for the fundamental Noxon band, obtained via EXOCROSS using the DUO calculated Einstein coefficients at 313 K with a Voigt line profile (HWHM = 0.15 cm^{-1}). The intensities have been scaled relative to the most intense $Q(8)$ transition. There is a systematic error in the line positions calculated by DUO $\sim 7 \text{ cm}^{-1}$, which is attributed primarily to the fact that the calculations do not include the strongly coupled excited $C^3\Pi_g$ state.³⁰ Due to the number of couplings required for a complete treatment of the open-shell O_2 molecule the full rovibronic spectrum, including such highly excited states will be the focus of a future publication. Consequently, and for the sake of simplicity, no empirical refinement of the PECs is performed in the present work. Nonetheless, the relative line positions and intensities are in good agreement with those measured by Fink *et al.*¹⁰²,

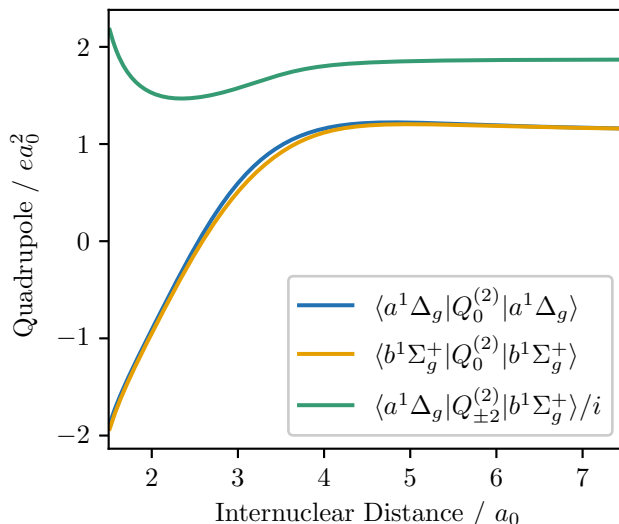


FIG. 11. Diagonal quadrupole moment curves in a.u. (ea_0^2) for the $a^1\Delta_g$ and $b^1\Sigma_g^+$ electronic states of O_2 obtained via MRCI calculations with a aug-cc-pV6Z basis set.

and demonstrate the validity of the approach for open-shell diatomic systems and excited electronic states.

IV. CONCLUSIONS

Generic expressions for the electric quadrupole Einstein coefficients and matrix elements between arbitrary electronic states of (open-shell) diatomic molecules have been derived and implemented in the DUO spectroscopic code. The implementation is general, and allows for the creation of highly accurate *ab initio* and empirical spectroscopic models and line lists for an array of astrophysically important molecules. The work has been validated by reproducing highly accurate literature data for the homonuclear H_2 molecule, as well by comparison to the electronic emission spectrum of the O_2 Noxon band, and further demonstrated by the calculation of novel electric quadrupole spectra for the heteronuclear CO and HF molecules. The line lists for CO and HF have been included into the ExoMol database.

Through this calculation, we have shown that even for electric dipole-allowed systems, electric-quadrupole line intensities can often lie above the typically cutoff intensities used in spectroscopic databases, atmospheric retrievals and remote-sensing applications. For many

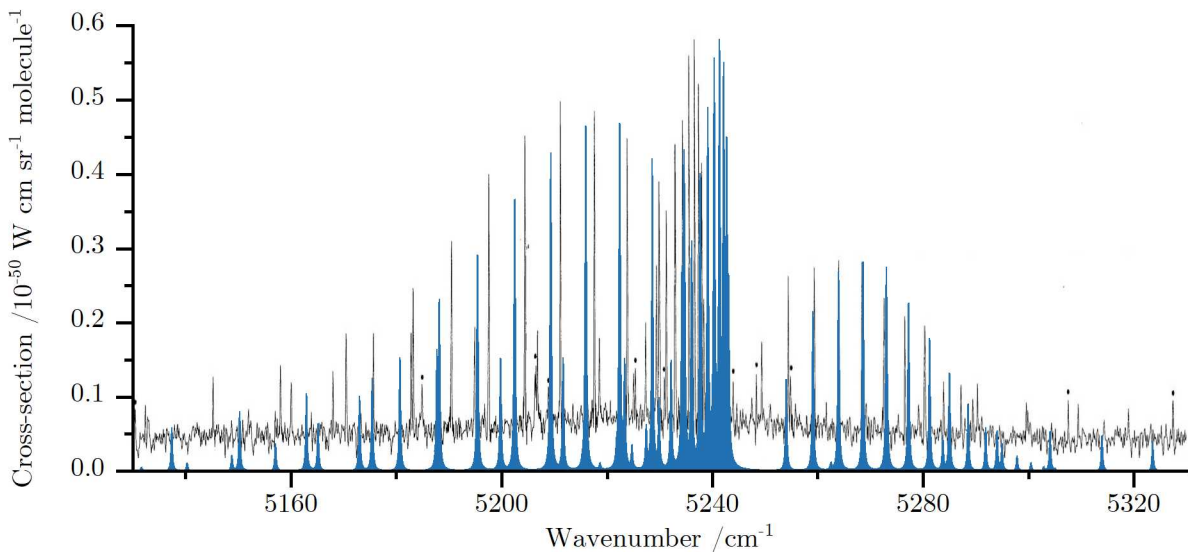


FIG. 12. Overlay of the DUO calculated O_2 Noxon emission cross-sections with the measured spectrum from Fink *et al.*¹⁰², scaled relative to the peak intensity of the $Q(8)$ transition. Cross-sections are calculated at $T = 313$ K with a Voigt profile (HWHM = 0.15 cm^{-1})

homonuclear systems where rovibrational, and many electronic, transitions are forbidden in the electric dipole approximation, calculation of the quadrupole intensities is crucial for producing accurate rovibronic line lists. Our goal is to provide accurate E2 and M1 line lists for electronic transitions of (open-shell) diatomic molecules such as O_2 , N_2 , S_2 , SO etc.

V. SUPPLEMENTARY MATERIAL

The supplementary material includes the spectroscopic models for H_2 , HF, CO and O_2 in the form of DUO input files; E2 line lists for H_2 , HF, CO and O_2 using the ExoMol format; examples of E2 room temperature spectra of these molecules with the upper and lower states fully assigned.

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VI. DATA AVAILABILITY

The data that supports the findings of this study are available within the article, its supplementary material and are also openly available at www.exomol.com.

VII. CONFLICT OF INTEREST

The authors have no conflicts to disclose.

Appendix A: Correlation of Molpro enumeration to term symbols

Tables XI and XII are versions of Tables I and II with the addition of MOLPRO enumerations for the irreducible representations. Which can be used to simplify the conversion of MOLPRO output data to Duo input.

TABLE XI. Irreducible representations for homonuclear symmetry groups, the functions that transform according to the irreducible representations, their MOLPRO enumeration, and corresponding components of electronic states.

Symmetry	Function	MOLPRO No.	Components
A_g	s	1	Σ_g^+ , $(\Delta_g)_{xx}$
B_{1g}	xy	4	Σ_g^- , $(\Delta_g)_{xy}$
B_{2g}	xz	6	$(\Pi_g)_x$
B_{3g}	yz	7	$(\Pi_g)_y$
A_u	xyz	8	Σ_u^- , $(\Delta_u)_{xy}$
B_{1u}	z	5	Σ_u^+ , $(\Delta_u)_{xx}$
B_{2u}	y	3	$(\Pi_u)_y$
B_{3u}	x	2	$(\Pi_u)_x$

TABLE XII. Irreducible representations for heteronuclear symmetry groups, the functions that transform according to the irreducible representations, their MOLPRO enumeration, and corresponding components of electronic states.

Symmetry	Function(s)	MOLPRO No.	Components
A_1	s, z	1	Σ^+ , Δ_{xx}
A_2	xy	4	Σ^- , Δ_{xy}
B_1	x, xz	2	Π_x
B_2	y, yz	3	Π_y

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