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# The vibrational Stark effect

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Expressions for the frequency and intensity of the fundamental-vibrational transitions of a polyatomic molecule in the presence of a uniform or nonuniform electric field are reported. They have been developed on the basis of perturbation theory and take into account, individually, first-order electrical and mechanical anharmonicity. They are more general than previously-used expressions, since terms which are quadratic in the field strength are included. As an example of their use and of their interpretative capability, they are applied to CO.

## I. INTRODUCTION

The Stark effect<sup>1</sup> is the generic name for the effect of an electric field on optical spectra. An electric field ( $F$ ) perturbs the vibration of a molecule and consequently alters its infrared spectrum and this is known as the vibrational Stark effect (VSE). The changes caused by the field to the frequency ( $\omega_n$ ) and intensity ( $A_n$ ) of a given fundamental vibrational transition ( $n \leftarrow 0$ ) are experimentally represented by the vibrational Stark tuning rate ( $\delta_{vE} = d\omega_n/dF$ , where  $\hbar\omega_n$  is the  $n$ th fundamental-vibrational transition energy in the presence of the field) and the fractional change in the infrared cross section with respect to the field [ $\delta_{SE} = A_n^{-1}(\partial A_n/\partial F)$ ].

The source of the perturbation may simply be that of an externally-applied field, or it may be a field induced by collisions, or a field induced by surrounding the molecule by point charges, or one emanating from chemisorption of the molecule on a metal surface, or it may lie in the fact that the molecule is trapped in a chemical cage. This variety of situations permits the vibrational Stark effect to be a rich field for exploration from both experimental and theoretical standpoints. In some cases, the effect is quite dramatic as with the appearance of formerly forbidden vibrational transitions; this was first noted by Condon,<sup>2</sup> and later reemphasized by Woodward,<sup>3</sup> and seen in the early experimental work by Crawford and co-workers<sup>4</sup> on the vibrational rotation absorption of H<sub>2</sub>. Since then, there have been many more experiments on all kinds of species and in all kinds of environments. Martí *et al.*<sup>5</sup> have drawn attention to some of the more recent ones; these include measurements at electrodes, in zeolites, and in special infrared cells.

Theoretical studies are important not only in their own right, as is the case with the calculation of any molecular property, but also because, when linked to the experimental results, they allow us to make inferences concerning the electric field of the molecular surroundings: for example, a transition-metal surface or a zeolite cage. One such attempt for the latter is the work of Goulay *et al.*<sup>6</sup>

For the calculation of the change in a fundamental-vibrational transition frequency  $(\Delta\omega)_n$  by an electric field, there are three quantum mechanical techniques which can be applied in the context of VSE. These are (a) the calcu-

lation of the potential energy with a Hamiltonian which includes the electric field with a fixed value ( $F$ ). The vibrational Schrödinger equation is then solved for the nuclear motion and different vibrational energies are obtained for different values of  $F$ . In the context of the present study, Bauschlicher<sup>7</sup> has used this approach to consider the effects of an electric field on  $\omega_n$  for a free CO molecule; he used a finite difference method to solve the vibrational Schrödinger equation; Caffarel *et al.*<sup>8</sup> and Andzelm *et al.*,<sup>9</sup> in their work on CO absorbed on Pd clusters, have used a quantum Monte Carlo method to solve the vibrational Schrödinger equation. In all cases, the results are a series of changes for a set of chosen field strengths. Alternatively, (b) the derivatives with respect to the normal coordinates ( $Q_n$ ) of the field-perturbed energies may be found analytically and directly without finding the perturbed vibrational energies. For self-consistent-field (SCF) calculations, evaluation of such derivatives is now rather routine<sup>10,11</sup> and coupled with the FG method of Wilson, Decius, and Cross<sup>12</sup> (i.e., diagonalization of the mass-weighted Cartesian second derivatives), the  $\omega_n$  are readily obtained. The electric field (with different fixed finite values) is incorporated in the Fock equation. Duran and co-workers have used this method for CH<sub>4</sub>,<sup>13</sup> H<sub>2</sub>O, NH<sub>3</sub>, HCHO, and C<sub>2</sub>H<sub>4</sub>,<sup>14</sup> and CO<sup>15</sup> and, by replacing the complete polyelectronic Hamiltonian by a semiempirical one, for a number of larger species.<sup>5</sup> Andzelm *et al.*<sup>9</sup> have taken the same route with a density functional technique in place of the SCF one, and used it in a study of CO on Pd clusters.

The final method (c) at our disposal is that of perturbation theory. Since this is the choice of the present study and the details of its application will follow in the next section, suffice it to say, at this stage, that the change to  $\omega_n$  by the field can be developed to different orders of the field strength and the results expressed in terms of the derivatives of various molecular electrical properties (dipole moments, polarizabilities, etc.) and spectroscopic constants (anharmonic force constants, etc.) of the unperturbed molecule. Bagus *et al.*,<sup>16</sup> for systems of CO and CN absorbed on Cu, determined the perturbation terms linear in  $F$  for  $\omega_n$ . The required derivatives were obtained from finite field calculations. Quadratic terms in  $F$ , requiring derivatives of the polarizability ( $\alpha$ ) were not considered. Pacchioni and Bagus<sup>17</sup> dealt with the question of CO on

Cu and Pd clusters with fields stemming from point charges. Lambert,<sup>18,19</sup> again with the same first-order perturbation expression, investigated CO on a Ni cluster and in an aqueous double layer; however, his parameters were adapted so as to be appropriate for an absorbed rather than a free species. Cohen de Lara and co-workers have also used limited perturbation-theoretic expressions (anharmonicity was ignored) to study CH<sub>4</sub> (Ref. 20) and CO<sub>2</sub> (Ref. 6) when they are embedded in a zeolite cage. For CO<sub>2</sub>, in particular, their results were in disaccord with experiment.

Calculations of changes to the fundamental transition intensities ( $A_n$ ) in the presence of an electric field are much less common. Nearly all calculations begin with the approximation that expresses  $A_n$  in terms of the derivative of the electric transition dipole moment with respect to the normal coordinate  $Q_n$ . This derivative can then be obtained analytically from field-perturbed SCF equations. This was done by Duran and co-workers for CO,<sup>15</sup> H<sub>2</sub>O, NH<sub>3</sub>, HCHO, and C<sub>2</sub>H<sub>4</sub> (Ref. 14) and certain larger species at the semi-empirical level.<sup>5</sup> Results were given as values for particular field strengths. On the other hand, one can, as is explored in detail in this work, use perturbation theory. To date, this has been done only in an incomplete manner; for example, Cohen de Lara and co-workers in their study of N<sub>2</sub><sup>21</sup> and CH<sub>4</sub>,<sup>22</sup> where no anharmonicity was taken into account, or by Lambert<sup>19</sup> for CO, where the effects of change in dipole moment which relate to a change in polarizability were not considered.

The perturbation-theoretic treatment of VSE which is given in Sec. II follows, in spirit, the work of Bishop and Kirtman,<sup>23</sup> on vibrational polarizabilities and hyperpolarizabilities. There are several advantageous aspects to the approach taken. Foremost is its general applicability: polyatomic as well as diatomic molecules can be treated, expressions for the perturbed frequencies and intensities can be found as a power series in  $F$ , and the coefficients of the series can be directly related to experimental quantities ( $\delta_{vE}$ ,  $\delta_{SE}$ ). Further, there is the possibility of greater understanding and clearer interpretation since the sources of the changes in  $\omega_n$  and  $A_n$  by the field can be identified. From the point-of-view of producing numbers, the general availability of the required parameters from standard computer packages,<sup>10</sup> makes this a straight-forward matter. These parameters may, of course, pertain to the free molecule or be adapted to suit a particular chemical environment. Finally, though a question of taste, many find results which are in the form of a compact mathematical expression to be more aesthetic than a table of numbers corresponding to a set of chosen field strengths.

The perturbations-theoretic treatment, given in Sec. II, differs from previous ones in that it is more complete. That is to say, both electrical and mechanical anharmonicity are taken into account (each individually up to first order); expressions are developed which include quadratic as well as linear terms in  $F$  (this, e.g., allows  $\delta_{vE}$  to be field dependent) and they can also be used where a nonuniform field is present. The common initial assumption that the intensity can be written in terms of  $\partial\mu/\partial Q_n$  rather than the fundamental-vibrational transition dipole moment is not

made. Because there have been several previous theoretical VSE investigations of CO, this molecule has been chosen as an *example* of the use of the formulated methodology. It should not be construed as a definitive calculation.

As with all the work mentioned so far, field directions have been tacitly considered to be related to molecule-fixed axis system. That is, the molecule is non-rotating and, experimentally, this comes closest to those cases where a molecule is absorbed on a surface or, perhaps, trapped in a cage. The expressions developed, however, can be simply extended, if necessary, to take into account rotation by using the classical orientational-averaging technique.<sup>24</sup> For H<sub>2</sub>, purely quantum-mechanical methods must be used and the theory for doing this has been given by Dows and Buckingham<sup>25</sup> and in the work of Poll and co-workers<sup>26</sup> on the perturbation of the rotational-vibrational levels of H<sub>2</sub> and its isotopes by point charges.

Reviews which contain certain useful background material for this article have been written by Ashley and Pons<sup>27</sup> (experimental), Hirschfelder *et al.*<sup>28</sup> (theoretical), Amos<sup>10</sup> (theoretical), Bishop<sup>24</sup> (theoretical), and Buckingham<sup>29</sup> (theoretical and experimental).

When, in this paper, atomic units are used, they are defined by<sup>30</sup>

$$\text{length}(a_0) = 4\pi\epsilon_0\hbar^2/m_e e^2 \cong 0.529\,177\,\text{\AA},$$

$$\text{energy}(E_h) = \hbar^2/m_e a_0^2 \cong 4.359\,75 \times 10^{-18}\,\text{J},$$

$$\text{mass}(m_e) \cong 5.485\,80 \times 10^{-4}\,\text{u},$$

$$\text{electric field} = e/4\pi\epsilon_0 a_0^2 \cong 5.142\,21 \times 10^{11}\,\text{Vm}^{-1},$$

$$\begin{aligned} \text{dipole moment} &= ea_0 \cong 8.478\,36 \times 10^{-30}\,\text{Cm} \\ &\cong 2.541\,75\,\text{D}. \end{aligned}$$

Circular frequencies ( $\omega$ ) are defined such that  $\hbar\omega$  is in units of  $E_h$  and the equivalence  $E_h \cong 219\,474.6\,\text{cm}^{-1}$  can be made. Intensities are usually given in  $\text{km mol}^{-1}$  with

$$A_n = (4\pi\epsilon_0)^{-1} (2\pi N_A / 3\hbar c^2) g_n \mu_n^2 \omega_n \quad (1)$$

where  $\mu_n$  is the  $n$ th fundamental-vibrational transition dipole moment and  $g_n$  the degeneracy of the  $n$ th fundamental vibrational mode; we can also write

$$g_n \mu_n^2 = (\mu_x)_n^2 + (\mu_y)_n^2 + (\mu_z)_n^2$$

If  $\mu_n$  and  $\omega_n$  are in atomic units then

$$A_n = 3.5540 \times 10^6 g_n \mu_n^2 \omega_n \quad (2)$$

for  $A_n$  to be in  $\text{km mol}^{-1}$ . In the harmonic oscillator approximation, Eqs. (1) and (2) become

$$\begin{aligned} A_n &= (4\pi\epsilon_0)^{-1} (\pi N_A / 3c^2) g_n (\partial\mu/\partial Q_n)^2 \\ &\cong 1.1770 \times 10^6 g_n (\partial\mu/\partial Q_n)^2. \end{aligned} \quad (3)$$

## II. THEORY

First of all we will consider the effect of a non-uniform electric field on the *frequency* of a fundamental-vibrational

transition of a polyatomic molecule. The perturbation to the vibrational Hamiltonian due to the field(s)  $F$  may be written as

$$H' = -\mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{3}\Theta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{6}\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{3}A_{\alpha,\beta\gamma} F_\alpha F_\beta F_\gamma + \dots \quad (4)$$

where  $\mu_\alpha$  and  $\Theta_{\alpha\beta}$  are the dipole moment and quadrupole moment functions;  $\alpha_{\alpha\beta}$ ,  $\beta_{\alpha\beta\gamma}$  and  $A_{\alpha,\beta\gamma}$  are the polarizability, first hyperpolarizability, and dipole-quadrupole polarizability, respectively. The greek subscripts  $\alpha, \beta, \dots$  denote vector or tensor components and can be equal to  $x, y, z$  (a molecular-based axis system); a repeated subscript denotes a summation over all three Cartesian components;  $F_\alpha$  and  $F_{\alpha\beta}$  are the electric field and field gradient.

The change in fundamental vibrational frequency is related to the change in the energy difference between the  $n$ th fundamental-vibrational level and the ground state and according to perturbation theory this is

$$\hbar(\Delta\omega)_n = \Delta(E_n - E_0) = \langle n | H' | n^F \rangle - \langle 0 | H' | 0^F \rangle, \quad (5)$$

where  $|n^F\rangle$  and  $|0^F\rangle$  are the field-perturbed vibrational wave functions for the fundamental ( $n$ ) and ground vibrational states, respectively.

To evaluate the quantities in Eq. (5), we express the field-perturbed wave functions  $|n^F\rangle$  and  $|0^F\rangle$  in terms of the unperturbed ones. Since we require only terms in  $(\Delta\omega)_n$  up to  $F^2$ , we need only use first-order perturbation theory.<sup>28</sup> The first-order wave functions introduce the vibrational polarizabilities<sup>23,24</sup>  $\alpha_{\alpha\beta}^v(n)$  and  $\alpha_{\alpha\beta}^v(0)$  and the complete expression is

$$\begin{aligned} \hbar(\Delta\omega)_n = & -(\Delta\mu_\alpha)F_\alpha - \frac{1}{2}(\Delta\alpha_{\alpha\beta})F_\alpha F_\beta - \frac{1}{3}(\Delta\Theta_{\alpha\beta\gamma})F_\alpha F_\beta F_\gamma \\ & - \frac{1}{3}(\Delta A_{\alpha,\beta\gamma})F_\alpha F_\beta F_\gamma - \frac{1}{2}[\alpha_{\alpha\beta}^v(n) - \alpha_{\alpha\beta}^v(0)]F_\alpha F_\beta \end{aligned} \quad (6)$$

where for the electric properties ( $P$ )

$$(\Delta P) = \langle n | P | n \rangle - \langle 0 | P | 0 \rangle. \quad (7)$$

To determine these expectation values, we initially use the harmonic-oscillator approximation and then augment it by incorporating, individually, first-order electrical and mechanical anharmonicity. The former means writing any electric property as

$$P = P^0 + \sum_a (\partial P / \partial Q_a) Q_a + \frac{1}{2} \sum_{a,b} (\partial^2 P / \partial Q_a \partial Q_b) Q_a Q_b, \quad (8)$$

where  $Q_a$  are the normal coordinates and denoting the second derivatives as the first-order terms. The latter means expressing the potential energy as

$$V = V^0 + \frac{1}{2} \sum_a \lambda_a Q_a^2 + \frac{1}{6} \sum_{a,b,c} f_{abc} Q_a Q_b Q_c \quad (9)$$

where  $f_{abc}$  are the anharmonic force constants; these cubic terms will be taken as the first-order ones. A simplified notation will be convenient for the derivatives of the electrical properties ( $\partial P / \partial Q_a$ ), etc., namely  $(P/a)$ ,  $(P/ab)$ , etc., or, more specifically, for  $P = \mu_\alpha$  and  $P = \alpha_{\alpha\beta}$  we will write  $(\alpha/a)$ ,  $(\alpha/ab)$ , and  $(\alpha\beta/a)$ ,  $(\alpha\beta/ab)$ .

In the harmonic oscillator approximation  $\alpha_{\alpha\beta}^v(n)$  and  $\alpha_{\alpha\beta}^v(0)$  are the same and the first-order electrical and mechanical anharmonic corrections are zero,<sup>23</sup> so these terms, to this order, can now be dropped, the remaining  $(\Delta P)$  terms may be evaluated from the integrals in Appendix III of Ref. 12. The final result is

$$(\Delta P) = (\hbar/2\omega_n) [(P/nn) - \sum_a f_{ann} (P/n) \omega_n^{-2}] \quad (10)$$

where the first term in the square brackets results from the electrical anharmonicity and the second one from the mechanical anharmonicity. In this context, and later, the vibrational frequencies  $\omega_n$  and  $\omega_a$  are the harmonic ones. Equations (6) and (10), together, define the change in frequency of a fundamental-vibrational transition when a molecule is placed in an electric field. For a diatomic molecule, Eq. (10) becomes simply

$$(\Delta P) = (\hbar/2\omega_n) [(P/nn) - f_{nnn} (P/n) \omega_n^{-2}]. \quad (11)$$

To approximate, via perturbation theory, the change in the intensity  $A_n$ , of the  $n$ th fundamental-vibrational transition, we begin with Eq. (2). This means that we must determine the shift in  $\mu_\alpha^2 \omega_n$ . We have already considered the shift in  $\omega_n$  and are therefore left with finding  $\langle 0^F | \mu_\alpha^F | n^F \rangle$  and  $\langle 0 | \mu_\alpha | n \rangle$  to first order in the anharmonicities.  $\mu_\alpha^F$  is defined by

$$\mu_\alpha^F = \mu_\alpha + \alpha_{\alpha\beta} F_\beta + \frac{1}{2} \beta_{\alpha\beta\gamma} F_\beta F_\gamma + \frac{1}{3} A_{\alpha,\beta\gamma} F_\beta F_\gamma \quad (12)$$

For determination of the term in  $\langle 0^F | \mu_\alpha^F | n^F \rangle$  which is linear in  $F$ , we follow in the same fashion as for  $\Delta\omega_n$ , but for the higher-order terms in  $F$  we restrict ourselves to the harmonic oscillator approximation only.

The unperturbed transition dipole integral, to first order in both anharmonicities, separately, is found to be

$$\langle 0 | \mu_\alpha | n \rangle = (\hbar/2\omega_n)^{1/2} (\alpha/n). \quad (13)$$

The equivalent field-perturbed integral is more complex. First,  $|0^F\rangle$  and  $|n^F\rangle$  must be determined to second order in the perturbation  $-\mu_\alpha F_\alpha$  (assuming, for the moment, a uniform field); the rest of the perturbation in Eq. (4), if we consistently limit ourselves to the electrical and mechanical harmonic oscillator approximation for the nonlinear terms in  $F$  in  $\langle 0^F | \mu_\alpha^F | n^F \rangle$ , will appear only in  $\langle 0 | \mu_\alpha^F | n \rangle$ . Once  $|0^F\rangle$  and  $|n^F\rangle$  have been found, using standard perturbation-theoretic formulas,<sup>28</sup> the anharmonic corrections to the harmonic oscillator approximation can be made and an expression for the complete integral found. This requires great care in identifying the intermediate vibrational states which occur in the  $|0^F\rangle$  and  $|n^F\rangle$  expansions. That done, the actual integration over the harmonic oscillator wave functions is trivial. The final result is

$$\begin{aligned} \langle 0^F | \mu_\alpha^F | n^F \rangle = & (\hbar/2\omega_n)^{1/2} (D_1 + D_2 F_\beta + \frac{1}{2} D_3 F_\beta F_\gamma \\ & + \frac{1}{3} D_4 F_\beta F_\gamma), \end{aligned} \quad (14)$$

where

$$D_1 = (\alpha/n), \quad (15)$$

$$D_2 = (\alpha\beta/n) + (\alpha/n)(\beta/nn)(2\omega_n)^{-2} + \Sigma_a(\alpha/an) \\ \times (\beta/a)\omega_a^{-2} + \Sigma_{a \neq n}(\alpha/a)(\omega_a^2 - \omega_n^2)^{-1} \\ \times [(\beta/an) - \Sigma_b f_{abn}(\beta/b)\omega_b^{-2}], \quad (16)$$

$$D_3 = (\alpha\beta\gamma/n) - \hbar^{-1}(\alpha/n)\Sigma_a(\beta/a)(\gamma/a)\omega_a^{-3}, \quad (17)$$

$$D_4 = (\alpha\beta\gamma/n). \quad (18)$$

It is informative to identify the source of the contributions to these  $D_i$  terms. In all cases, the initial term in  $D_i$  originates from  $\mu_\alpha^F$  and is the same as that which would be given in the harmonic oscillator approximation since the first-order anharmonic corrections are zero.  $D_3$  and  $D_4$  have only been found at the level of the harmonic oscillator approximation; the second term of  $D_3$  stems from the second order terms in the expansion of  $|0^F\rangle$  and  $|n^F\rangle$ —this term would not appear if the conventional intensity approximation, Eq. (3), were used; it is, however, not negligible. The second and third terms and the first part of the fourth term in  $D_2$  arise from the first-order expansion of  $|0^F\rangle$  and  $|n^F\rangle$  coupled with the first-order electrical anharmonicity in  $(\partial^2 P/\partial Q_a \partial Q_b)$ ; the second part of the fourth term in  $D_2$  is similar to the first part but instead accounts for the mechanical anharmonicity.

In summary, Eqs. (6), (11), (14)–(18) provide a set of working equations, at a consistent level of approximation, which allow changes to  $\omega_n$  and  $\langle 0|\mu_\alpha|n \rangle$  due to an electric field to be evaluated. Combined together they provide the means of determining the changes to the intensity of a fundamental-vibrational transition. The form of the expressions is such that the sources of the changes (anharmonicities, etc.) can be identified.

For diatomic molecules, with a uniform field along the internuclear axis ( $z$ ), the frequency shift will be

$$(\Delta\omega)_n = (2\omega_n)^{-1}[(z/nn) - f_{nnn}(z/n)\omega_n^{-2}](-F_z) \\ + (2\omega_n)^{-1}[(zz/nn) - f_{nnn}(zz/n)\omega_n^{-2}] \\ \times (-\frac{1}{2}F_z^2). \quad (19)$$

Again, the shift  $(\Delta\omega)_n$  is to the fundamental frequency and the  $\omega_n$  on the left-hand side is the harmonic frequency. The linear term is expressed in  $(-F_z)$ , since the field direction is usually defined with respect to the molecular dipole moment in such a way that a positive field increases  $(\Delta\omega)_n$ . For the change in the vibrational transition integral, we have for a diatomic molecule:

$$\langle 0^F|\mu_\alpha^F|n^F\rangle = (\hbar/2\omega_n)^{1/2}[(z/n) - \{(zz/n) + (5/4)(z/n) \\ \times (z/nn)\omega_n^{-2}\}(-F_z) + \{(zzz/n) \\ - \hbar^{-1}(z/n)^3\omega_n^{-3}\}(\frac{1}{2}F_z^2)]. \quad (20)$$

The form of Eq. (19) follows, transparently, the well-known expression<sup>24</sup> for zero-point-vibrational averaging. In comparison with previous work, over and above the use of Eq. (3) rather than Eq. (2), there are certain other points which may now be made. Lambert,<sup>19</sup> Bagus and co-workers<sup>16,17</sup> used only the first (linear) term in Eq.

TABLE I. Molecular properties for CO in atomic units.

	Set I <sup>a</sup>	Set II <sup>c</sup>
$\omega_n$	$9.9638 \times 10^{-3}$	$1.043 \times 10^{-2}$
$f_{nnn}$	$-3.206 \times 10^{-6}$ <sup>b</sup>	$-3.54 \times 10^{-6}$
$\partial\mu_z/\partial Q_n$	$5.660 \times 10^{-3}$	$9.326 \times 10^{-3}$
$\partial^2\mu_z/\partial Q_n^2$	$-1.92 \times 10^{-6}$	$3.049 \times 10^{-5}$
$\partial\alpha_{zz}/\partial Q_n$	$8.502 \times 10^{-2}$ <sup>c</sup>	$8.502 \times 10^{-2}$
$\partial^2\alpha_{zz}/\partial Q_n^2$	$5.457 \times 10^{-4}$ <sup>c</sup>	$5.457 \times 10^{-4}$
$\partial\beta_{zz}/\partial Q_n$		$8.209 \times 10^{-2}$

<sup>a</sup>With the exceptions noted, these values are taken from Ref. 7.

<sup>b</sup>Derived from the spectroscopic constants  $\alpha_e$ ,  $B_e$ , and  $\omega_e$  given in Ref. 7.

<sup>c</sup>Based on a SCF calculation using a (10s 6p 4d) basis set for both C and O contracted to [5s 3p 2d]. This basis set was taken from Ref. 31.

(19), Cohen de Lara and co-workers<sup>6,20</sup> neglected the effects of mechanical anharmonicity and this may well explain the disaccord with experiment which they found.<sup>6</sup> As for the intensity formula, Eq. (20), Lambert's expression<sup>19</sup> corresponds to just the third term in  $D_2$  in Eq. (17) and Cohen de Lara and co-workers's treatment<sup>21,22</sup> was limited to simply the first term in  $D_2$ . Finally, the form of the expressions given above, in terms of powers of  $F$ , allows for easy association of the coefficients with the experimental parameters ( $\delta_{vB}$ ,  $\delta_{SE}$ ). It may be noted that for a diatomic molecule, at this level of approximation, there are no mechanical-anharmonic contributions to the field-perturbed transition dipole moment in Eq. (20).

### III. AN EXAMPLE: CO

As an example of the application of the theory given in the preceding section, the vibrational Stark effect for CO had been chosen. For this molecule there are other treatments<sup>7,15</sup> available with which comparison can be made. The intention is not to provide definitive values for the frequency and intensity shifts for CO but rather to assess the contributions to the shifts and identify their source.

First, we assemble the required parameters. Initially we take a set, augmented by values of  $\partial\alpha_{zz}/\partial Q$  and  $\partial^2\alpha_{zz}/\partial Q^2$ , from the work of Bauschlicher.<sup>7</sup> We do this in order to make a comparison with his finite-field results for  $(\Delta\omega)_n$ . These parameters are called Set I in Table I. The normal coordinate (using atomic units of mass) for CO is given by

$$Q = \mu^{1/2}(r - r_e) = 111.79(r - r_e)$$

with  $r$  being the internuclear separation and  $r_e = 2.132 a_0$ . Equation (19) then reads, in atomic units, as

$$(\Delta\omega)_n = 50.182(-1.92 \times 10^{-6} + 1.824 \times 10^{-4})(-F_z) \\ + 50.182(5.46 \times 10^{-4} + 2.740 \times 10^{-3}) \\ \times (-\frac{1}{2}F_z^2) \quad (21)$$

and, in  $\text{cm}^{-1}$ , as

$$(\Delta\omega)_n = 1.99 \times 10^3(-F_z) - 1.81 \times 10^4(F_z^2). \quad (22)$$

Values of  $(\Delta\omega)_n$  using the latter equation are given for three different field strengths in Table II, along with the

TABLE II. Values of  $(\Delta\omega)_n$  in  $\text{cm}^{-1}$  for CO, using Eq. (19) and parameter Set I; these are compared with those of Bauschlicher (Ref. 7).

$-F_z$ (a.u.)	This work	Bauschlicher (Ref. 7)
0.005	9.50	9.62
0.01	18.09	18.11
0.015	25.78	25.36

corresponding values found by Bauschlicher. The agreement is very good. Of interest is the fact that it is the mechanical-anharmonic term which dominates both the linear and quadratic terms in  $F_z$  and that the quadratic contribution, though small, is significant and will lead to a field dependence in the Stark tuning rate  $\delta_{vE}$ .

To make a comparison of the values of the frequency and intensity shifts given by the formulas in this work with those values determined by Andrés *et al.*,<sup>15</sup> the latter's values have been fitted, for the two basis sets which they used (DZ) and DZP), to

$$(\Delta\omega)_n = a(-F_z) + bF_z^2 \quad (23)$$

and

$$(\Delta A)_n = A(-F_z) + BF_z^2. \quad (24)$$

Values of  $a, b, A$ , and  $B$  are given in Table III and compared with those found directly from the perturbation-theoretic formulas. Also in Table III, the unperturbed  $\omega$  and  $A$  values are shown. Bearing in mind that the basis set<sup>31</sup> used in this work is different, the agreement is gratifying, the only exception being the coefficient  $B$ , but this term is both small and very sensitive to both basis set choice and the values of the derivative parameters. For  $(\Delta\omega)_n$  in both the linear and quadratic terms in  $F_z$  it is again the mechanical-anharmonic contribution which dominates (by an order of magnitude).

Using the parameters of Set II of this work (Table I), the perturbed transition dipole moment is

$$\langle 0^F | \mu_\alpha^F | n^F \rangle = (\hbar/2\omega_n)^{1/2} (9.326 \times 10^{-3} + 8.829 \times 10^{-2} F_z - 3.164 \times 10^{-1} F_z^2) \quad (25)$$

TABLE III. Coefficients for Eqs. (23) and (24) for CO, with frequency and intensity shifts in  $\text{cm}^{-1}$  and  $\text{km mol}^{-1}$ , respectively, and field strengths in atomic units, together with the unperturbed values of  $\omega_n$  and  $A_n$ .

	Ref. 15 DZ basis	Ref. 15 DZP basis	This work parameter Set II
$a$	$3.7 \times 10^3$	$3.3 \times 10^3$	$3.514 \times 10^3$
$b$	$-2 \times 10^4$	$-2 \times 10^4$	$-1.743 \times 10^4$
$A$	$-3.2 \times 10^3$	$-2.9 \times 10^3$	$-2.69 \times 10^3$
$B$	$1 \times 10^4$	$1 \times 10^4$	$-2.30 \times 10^3$
$\omega_n$	2265	2424	2289
$A_n$	175	164	154.6

and the coefficient of the linear term is largely dominated by the polarizability derivative  $(\alpha\beta/n)$ . The perturbed fundamental-vibrational frequency (in  $\text{cm}^{-1}$ ) is similarly given by

$$\omega_n^F = 2289 - 3.514 \times 10^3 F_z - 1.743 \times 10^4 F_z^2. \quad (26)$$

This leads to the fact that the linear term (in  $F_z$ ) in  $A_n$  is dominated (by an order of magnitude) by a product of the constant and the linear term in the perturbed transition dipole moment and thereby, by implication, by the polarizability derivative. The quadratic term in  $A_n$  is a rather delicate balance of contributions; the two most important ones are of similar size but of opposite sign.

#### IV. SUMMARY

As an alternative to finite-field calculations of the vibrational Stark effect, perturbation-theoretic formulas have been developed at a consistent level of approximation. These formulas require knowledge of the derivatives of the dipole moment and polarizability functions with respect to the normal coordinates; quantities which are now readily available from standard quantum-chemical computer packages. The formulas have been applied to CO and it is seen that the major contribution to the shifts in fundamental-vibrational frequencies and intensities caused by an electric field may be identified. It has also been shown that the formulas lead to results which are compatible with previously-published finite-field calculations for CO.

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