Theoretical study of the second-order vibrational Stark effect

JOSEP MARTÍ*, JOSEP M. LUIS and MIQUEL DURAN
Institute of Computational Chemistry and Department of Chemistry, University of Girona, 17071 Girona, Catalonia, Spain

(Received 20 February 1998; revised version accepted 15 April 1999)

The behaviour of the harmonic infrared frequency of diatomic molecules subjected to moderate static uniform electric fields is analysed. The potential energy expression has been developed as a function of a static uniform electric field, which brings about a formulation describing the frequency versus field strength curve. With the help of the first and second derivatives of the expressions obtained, which correspond to the first- and second-order Stark effects, it was possible to find the maxima of the frequency versus field strength curves for a series of molecules using a Newton–Raphson search. A method is proposed which requires only the calculation of a few energy derivatives at a particular value of the field strength. At the same time, the expression for the dependence of the interatomic distance on the electric field strength is derived and the minimum of this curve is found for the same species. Derived expressions and numerical results are discussed and compared with other studies.

1. Introduction

The vibrational Stark effect (VSE) has become an important subject of study in the field of heterogeneous catalysis and surface chemistry. The behaviour of the vibrational spectra of species chemisorbed on certain metallic surfaces or in other materials like zeolites can be explained in part by considering that in these situations the main perturbation affecting the adsorbed molecules is a static uniform electric field. There have been many theoretical studies dealing with the calculation of the parameters related to VSE [1–10], and experimental evaluations of these parameters have been carried out by several authors using special spectroscopic techniques [11–16].

There are two main parameters related to the experimental study of the VSE, the Stark tuning rate ($\delta_{SE}$), and the infrared cross-section change ($\delta_{SE}$). $\delta_{SE}$ represents the rate change of the position of the infrared bands with the electric field strength, while $\delta_{SE}$ is the rate change of the intensity of the infrared bands with the electric field strength.

In general, the VSE is related to $\delta_{SE}$. One can express this value as the first derivative of the infrared frequency with respect to the field strength:

$$\delta_{SE} = \left(\frac{d\nu}{dF}\right)_{F=0}.$$  \hspace{2cm} (1)

Knowledge of this parameter lets us obtain the frequency shift experienced by the particular vibrational mode for which it has been calculated, provided that the field strength is small enough. It is very important to emphasize that this approximation is valid only for low values of the field strength, and that the behaviour of the frequency versus field strength curve is not linear across the range of fields found in certain experimental situations.

Various studies have dealt with frequency calculations of molecules influenced by strong electric fields [17–20]. The tendency of the infrared frequency value of certain species to increase or decrease in the presence of a uniform electric field is shown to depend on the strength of this field. As an example of this phenomenon, Hermansson [17] carried out a theoretical study of the OH stretching frequency of bounded OH$^-\,$ ion, involving various interacting species (ions, hydrogen bonded molecules, point charges) and a uniform electric field. One of the experimental observations concerning these systems is that frequency up- and downshifts are found depending on the molecular interaction strength. In spite of the fact that the electric fields involved in chemical interactions are far from uniform, the general trends followed by these systems can be predicted using a uniform electric field. Thus Hermansson [17] performed ab initio calculations of the frequency versus field strength curves which show them to have a parabolic shape with a maximum located not far from the origin, i.e., from low to moderate field strengths (0.01–0.1 au). Subsequently, Hermansson [18–20] tried also to establish a correlation between the behaviour of the frequencies and that of the dipole moment derivative (w.r.t. atom displacements along a normal mode $Q$), arguing
that, within an appropriate theoretical approach, \( \frac{d\mu}{dQ} \) vanishes when the frequency maximum is reached.

Recently our group has developed a methodology for studying the vibrational contributions to the electrical properties from which we can obtain compact expressions for these contributions [21–23]. This formulation can be used also for the study of the vibrational Stark effect. In fact, such a methodology has already been used for this purpose by other authors. For instance, Lambert [15], in an early study, combined experimental work with theoretical development based on the expansion of the energy in terms of the field strength and the internuclear distance in the case of the CO molecule. A different approach was used by Bishop [24], who obtained the same set of formulae using perturbation theory. Finally, our group studied the basis set and level of calculation dependence of the electrical properties of the CO molecule using the series expansion model where first-order Stark effect results were also reported [21]. Both approaches, perturbational and expansion in Taylor series, were compared and discussed by Martí and Bishop [25].

The aim of the present paper is to use the methodology developed in [21] and [22] to analyse the vibrational Stark effect when moderate fields are present, and to establish the condition, in terms of molecular properties, holding at the maximum of the frequency versus field curve. In a similar way, the condition for the minimum of the internuclear distance versus field curve will be studied in order to compare the nature of these two singular points. Moreover, we have tried to minimize the task of calculating higher order energy derivatives, thus permitting fast and accurate determination of maxima of \( \nu_c \).

2. Methodology

The energy of a molecule subjected to a uniform electric field can be expressed by the expansion

\[
V = V_0 - \sum_i \mu_i F_i - \frac{1}{2} \sum_{i,j} \alpha_{ij} F_i F_j - \frac{1}{3!} \sum_{i,j,k} \beta_{ijk} F_i F_j F_k - \cdots, \tag{2}
\]

where \( F_i \) represents the component of the static, uniform electric field applied along the \( i \) coordinate axis, and the coefficients \( \mu, \alpha, \beta \) stand for the electrical properties of the molecule, namely, dipole moment, polarizability and first hyperpolarizability. Every electrical property is in turn a function of the molecular geometry. Taking this into account, one can expand the potential energy of a molecule as a power series of the field strength and the geometrical parameters. For the simplest case, i.e., for a diatomic molecule under the effect of an electric field applied along its molecular axis, one can write the molecular energy as a double power series:

\[
V(Q,F) = a_{00} + a_{10} Q + a_{20} Q^2 + a_{30} Q^3 + a_{40} Q^4 + \cdots
+ (a_{01} + a_{11} Q + a_{21} Q^2 + a_{31} Q^3) F + \cdots
+ (a_{02} + a_{12} Q + a_{22} Q^2) F^2 + \cdots
+ (a_{03} + a_{13} Q) F^3 + \cdots
+ a_{04} F^4 + \cdots
\]

\[
\vdots, \tag{3}
\]

where \( F \) stands for the electric field strength, \( Q \) is the weighted displacement of the stretching normal coordinate from its field-free equilibrium position (\( Q = m_{1/2} (R - R_e) \)), where \( R \) and \( R_e \) are, respectively, the current and the equilibrium interatomic distances, and \( m \) stands for the reduced mass of the system, and the coefficients \( a_{ij} \) are the derivatives of the energy with respect to the coordinate displacement and to the electric field strength. These coefficients correspond to the following notation:

\[
a_{ij} = \frac{1}{\eta F} \left( \frac{\partial^{(i+j)} V}{\partial Q^i \partial F^j} \right)_{Q=0,F=0}. \tag{4}
\]

It is very important to keep in mind that this last derivative might also be evaluated at \( F \) and \( Q \) different from zero, i.e., expansion (3) can be performed also at any field strength and position.

Applying the equilibrium condition \( (\partial V/\partial Q)_F = 0 \) to equation (3), one can find the expression for the variation of equilibrium internuclear distance with field strength which, to second order in the field strength, is

\[
Q_{eq}(F) = -\frac{a_{11}}{2a_{20}} F - \left( \frac{a_{12}}{2a_{20}} - \frac{a_{11} a_{21}}{2a_{20}^2} + \frac{3 a_{30} a_{11}^2}{8 a_{20}^3} \right) F^2 + \cdots \tag{5}
\]

Here \( a_{10} \) (gradient at zero field) has been set to zero because the expansion is performed at the optimized interatomic distance. Substitution of \( Q_{eq}(F) \) in general potential expansion (3) yields the expression for the equilibrium energy of the molecule with respect to the field strength. This resulting expansion is of utmost importance for the study of the nuclear contributions to the electrical properties. In the coefficients of the different powers of \( F \) one finds not only the electronic part of the electrical properties \( (a_{ij}) \) but also expressions corresponding to the so-called nuclear relaxation contributions [21, 22].
Another part of the nuclear contributions to electrical properties is that arising from the vibrational energy of the molecule. Derivation of the harmonic force constant expression from equation (3) and substitution of the general coordinate $Q$ by the equilibrium one given in equation (5) results in the expression of the force constant as a function of the field strength at the equilibrium position (otherwise such a calculation would lack physical sense).

$$k_e(F) = \left(\frac{\partial^2 V}{\partial Q^2}\right)_{Q_0(F)} = 2a_{20} \left(2a_{21} - \frac{3a_{11}a_{30}}{a_{20}}\right)F + \left(2a_{22} - \frac{3a_{12}a_{30}}{a_{20}} - \frac{3a_{11}a_{31}}{a_{20}} - \frac{a^2_{21}}{2a_{20}}
+ \frac{3a_{11}a_{21}a_{30}}{a_{20}} + \frac{3a_{12}a_{40}}{a_{20}} - \frac{9a_{11}^2a_{30}}{4a_{20}^2}\right)F^2 + \cdots \tag{6}$$

Equation (6) would be enough to accomplish the main goal of this work. However, one can go further and calculate the expression of the harmonic frequency $\nu_e$ by simply recalling the relation between this parameter and the force constant $k_e$:

$$\nu_e = \frac{1}{2\pi} \left(\frac{k_e}{m_e}\right)^{1/2}, \tag{7}$$

where $m_e$ stands for the reduced mass of the system. From this last expression it is possible to obtain the successive derivatives of $\nu_e$ from the derivatives of $k_e$. In particular, the first and second derivatives of $\nu_e$ are

$$\frac{d\nu_e}{dF} = \frac{\nu_e}{2k_e} \frac{dk_e}{dF}. \tag{8a}$$

and

$$\frac{d^2\nu_e}{dF^2} = \frac{\nu_e}{2k_e} \left(\frac{d^2k_e}{dF^2} - \frac{1}{2k_e} \left(\frac{dk_e}{dF}\right)^2\right). \tag{8b}$$

Taking into account the expression of the first derivative of $\nu_e$ (equation (8a)), it is obvious that the maxima of $k_e$ and $\nu_e$ with respect to the field strength will coincide. Considering the two derivatives of equation (8), an expression for $\nu_e(F)$ analogous to that of $k_e(F)$ can be derived:

$$\nu_e(F) = \nu_e^0 + \frac{\nu_e^0}{2k_e^0} \left(2a_{21} - \frac{3a_{11}a_{30}}{a_{20}}\right)F + \nu_e^0 \times \left(2a_{22} - \frac{3a_{12}a_{30}}{a_{20}} - \frac{3a_{11}a_{31}}{a_{20}} - \frac{a^2_{21}}{2a_{20}}
+ \frac{9a_{11}a_{21}a_{30}}{2a_{20}} + \frac{3a_{12}a_{40}}{a_{20}} - \frac{27a_{11}^2a_{30}}{8a_{20}^2}\right)F^2 + \cdots \tag{9}$$

where $\nu_e^0$ and $k_e^0$ stand, respectively, for the harmonic frequency and the force constant in the absence of any electric field. This last expression is the key for the study of the vibrational Stark effect. The coefficient in $F$ represents the classic first-order Stark effect, while the coefficient in $F^2$ is what can be labelled as the second-order Stark effect.

In order to calculate the maximum of the $k = k(F)$ curve one can indeed make use of equation (6) which involves the set of coefficients $a_{ij}$ calculated by expanding the energy expression about $F = 0$ and $Q = 0$. However, this involves the calculation of high order $a_{ij}$ coefficients, which can be very expensive depending on the polynomial truncation in equation (6).

In this paper we propose a slightly different, yet mathematically equivalent, approach. If one generalizes potential energy expansion (3) considering as the equilibrium geometry not that of $F_e = 0$, but that of a given nonzero field $F_e$, once the molecular geometry is optimized in presence of this new field, the expansion of the energy about this point can be expressed as

$$V(Q,F) = \sum_{i,j} a_{ij}^e Q^i F^j, \tag{10}$$

where $F$ represents now the difference between the total field $(F + F_e)$ and the equilibrium field $(F_e)$, and $Q$ is the difference between the equilibrium geometry at a field $F_e(R_{F=F_e})$ and the current geometry $R$. The new $a_{ij}$ coefficients correspond exactly to definition (4), although now the derivatives are not evaluated at $F = 0$, $R = R_{F=0}$, but at $F = F_e$ and $R_{F=F_e}$. In order to account better for these changes, the new coefficients will be labelled as $a_{ij}^e$. Given that all the theory developed for the case $F = 0$ (equations (5)–(9)) is still valid for the general case, the condition for the $k$ curve to have a maximum, i.e., $dk/dF = 0$, can be written as

$$2a_{21}^e = \frac{3a_{11}^e a_{50}^e}{a_{20}^2}. \tag{11}$$

Knowledge of the first- and second-derivative values of the $k_e$ versus field strength curve at any field strength permits the exact location of the maximum of this curve using the Newton–Raphson iterative procedure.
One must note that condition (11) holding for the maximum of the $k$ versus $F$ curve is not the same as that proposed in [18–20], where the condition for the existence of a maximum consists of the derivative of the dipole moment with respect to the nuclear displacement vanishing. In the formulation that we propose, this translates into the condition $a_{11}^0 = 0$. Differences from Hermansson’s paper [19] may be due to a misleading aspect of one of the terms taking part in the first-order Stark effect expression. The first derivative of the force constant with respect to the field can be expressed as the sum of two terms. One of these terms represents the variation of the force constant with respect to the field by taking the geometry constant, while the other term represents the change of the force constant with respect to the field due to the change of geometry under a constant field. This can be expressed mathematically as

$$\frac{dk}{dF} = \left(\frac{\partial k}{\partial F}\right)_Q + \left(\frac{\partial k}{\partial Q}\right)_F \frac{dQ}{dF}. \quad (12)$$

In the notation proposed, the first partial derivative in equation (12) corresponds to the term $2a_{11}^0$, which is not taken into account in Hermansson’s formulation. The second partial derivative in equation (12) corresponds to the first term accounting for mechanical anharmonicity in the energy expansion, which is equivalent to $6a_{30}$ in our notation. The total derivative of the normal coordinate with respect to the field strength can be extracted from equation (5) and, given that $a_{20}^e$ and $a_{30}^e$ do not vanish in the range of fields studied, the only possibility for this term to be null is that $a_{11}^e$ becomes zero, which is the maximum condition proposed by Hermansson [19].

The condition holding for the existence of a minimum of the equilibrium internuclear distance versus field strength can be determined in a way similar to that of the maximum of the force constant. Indeed, one can make use of equation (5), and truncate the polynomial properly. However, one can employ the same technique as in the case of $k$ and use the expansion of the equilibrium $Q$ at a field $F$ different from zero. The minimum condition for the internuclear distance curve will be that the first derivative of this curve vanishes:

$$\frac{a_{11}^e}{2a_{20}^e} = 0 \quad (13)$$

As the denominator has a nonzero value in the range of fields studied, this last equality is equivalent to $a_{11}^e = 0$, i.e., the dipole moment derivative is equal to zero at the minimum of the equilibrium geometry versus field curve. This condition can be checked in [20], table 4, where the field strengths that make the dipole moment derivative equal to zero are in general closer to the minimum of the bond length versus field strength curve than to the maximum of the corresponding frequency curve. As in the $k_e$ case, the minimum of the $R_e$ curve can be located following a Newton–Raphson search as long as we know the first and second derivatives of this curve at any field strength value.

### 3. Computational details

All calculations reported in this work have been performed at an *ab initio* SCF level with a 6-311+ + G(3df,3pd) basis set and the Gaussian 94 program [26], taking 6 Gaussians for the description of d orbitals and 10 for f orbitals. Molecular geometry has been optimized for every field using an extremely tight convergence criterion (r.m.s. force $< 10^{-6} \text{E}_h a_0^{-1}$). This program yields analytical results for $a_{20}^e$, $a_{01}^e$, $a_{11}^e$, $a_{02}^e$, $a_{12}^e$ and $a_{03}^e$ (through non-standard routes). Then, numerical differentiation of $a_{20}^e$, $a_{01}^e$, $a_{12}^e$ and $a_{03}^e$ with respect to normal coordinates yields $a_{20}^e$, $a_{01}^e$, $a_{12}^e$ and $a_{13}^e$, respectively. $a_{40}^e$ and $a_{31}^e$ are obtained by double numerical differentiation of $a_{20}^e$ and $a_{11}^e$. Since the main goal of the following sections is to apply the theoretical methodology developed, which is independent of the quality of wavefunctions used, the changes caused by inclusion of electron correlation would not modify the overall conclusions.

### 4. Results and discussion

The theory developed in the preceding section has been applied to the molecules HF, BH, HLi and CO. The first three species have been chosen because they have already been used in the study by Hermansson and Tepper [20], thus allowing for proper comparisons, while CO has been elected due to its relevance in experimental and theoretical vibrational Stark effect studies [4, 5, 7, 10, 11, 15, 16, 21, 24]. In general, the electric field orientation has been taken to stabilize the molecule, considering its dipole moment at zero field. This has not been the case for the CO molecule where, as is well known, at the SCF level its dipole moment is inverted in sign with respect to experiment. However, as demonstrated elsewhere [7], the molecule reverses the sign of its dipole moment upon application of an electric field, thus behaving correctly, as in the experimental situation; furthermore, $d\mu/dR$ is quite well reproduced at the Hartree–Fock level. Figure 1 presents the orientations with respect to the electric field vector of the different species studied, together with the sign convention used for the field.

The numerical results (tables 1–4) consist of the first and second total derivatives of the force constant and the equilibrium distance with respect to the electric field...
strength (equations (5), (6)). These values are reported for every field strength in the Newton–Raphson search of the maximum of \( k_e \) and the minimum of \( R_e \) (condition (11)). Field strengths at the critical points are obtained within the maximum precision permitted by the Gaussian program [26] default keywords, 0.0001 au.

In the case of the search for the maximum \( k_e \), the first-order Stark effect is listed together with its field and geometric contributions, as exposed in the methodology section (equation (12)). It is important to remark that in the present work we are interested in the study of only the maximum of the force constant and the minimum of

**Figure 1.** Relative orientations of the four molecules studied with respect to the electric field vector.

**Table 1.** Evolution of different molecular parameters in the Newton–Raphson search of the maximum of the force constant \( k_e \) and the minimum of the interatomic distance \( R_e \) with the electric field strength \( F_e \) for the FH molecule. 1S stands for the first-order Stark effect and 2S the second-order Stark effect; \( \nu_e \) is the harmonic frequency. FS and GS are the first and second terms in equation (11). \( F_e^{\pm} \) represents the strength of the field to be applied in the next search step. 1R and 2R stand, respectively, for the first and second derivatives of the interatomic distance with respect of the field strength. All quantities are expressed in au except the interatomic distances in Å and the frequencies in cm\(^{-1}\).

### Maximum of \( k_e \) search

<table>
<thead>
<tr>
<th>( F_e^{\pm} )</th>
<th>( R_e )</th>
<th>( k_e )</th>
<th>( \nu_e )</th>
<th>FS</th>
<th>GS</th>
<th>1S</th>
<th>2S</th>
<th>( F_e^{\pm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00000</td>
<td>0.89758</td>
<td>1.45116</td>
<td>4476</td>
<td>-0.25376</td>
<td>3.02958</td>
<td>-3.28334</td>
<td>-53.70927</td>
<td>-0.0611</td>
</tr>
<tr>
<td>-0.0611</td>
<td>0.88819</td>
<td>1.53856</td>
<td>4609</td>
<td>0.85055</td>
<td>0.11579</td>
<td>0.73476</td>
<td>-86.20110</td>
<td>-0.0526</td>
</tr>
<tr>
<td>-0.0526</td>
<td>0.88847</td>
<td>1.54180</td>
<td>4614</td>
<td>0.64486</td>
<td>0.60695</td>
<td>0.03791</td>
<td>-78.07295</td>
<td>-0.0521</td>
</tr>
<tr>
<td>-0.0521</td>
<td>0.88850</td>
<td>1.54181</td>
<td>4614</td>
<td>0.63348</td>
<td>0.63451</td>
<td>-0.00102</td>
<td>-77.64974</td>
<td>-0.0521</td>
</tr>
</tbody>
</table>

### Minimum of \( R_e \) search

<table>
<thead>
<tr>
<th>( F_e^{\pm} )</th>
<th>( R_e )</th>
<th>1R</th>
<th>2R</th>
<th>( F_e^{\pm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00000</td>
<td>0.89758</td>
<td>0.38528</td>
<td>5.96060</td>
<td>-0.0646</td>
</tr>
<tr>
<td>-0.0646</td>
<td>0.88819</td>
<td>-0.01189</td>
<td>7.46315</td>
<td>-0.0630</td>
</tr>
<tr>
<td>-0.0630</td>
<td>0.88819</td>
<td>-0.00006</td>
<td>7.32383</td>
<td>-0.0630</td>
</tr>
</tbody>
</table>

*a* 1S = FS−GS = (d\( k_e \)/d\( F_e \))\( F_e = F_e^{\pm} \); 2S = (d\(^2\)\( k_e \)/d\( F_e^2 \))\( F_e = F_e^{\pm} \); 1R = (d\( R_e \)/d\( F_e \))\( F_e = F_e^{\pm} \); 2R = (d\(^2\)\( R_e \)/d\( F_e^2 \))\( F_e = F_e^{\pm} \).

**Table 2.** Evolution of different molecular parameters in the Newton–Raphson search of the maximum of the force constant \( k_e \) and the minimum of the interatomic distance \( R_e \) with the electric field strength \( F_e \) for the BH molecule. 1S stands for the first-order Stark effect and 2S the second-order Stark effect; \( \nu_e \) is the harmonic frequency. FS and GS are the first and second terms in equation (11). \( F_e^{\pm} \) represents the strength of the field to be applied in the next search step. 1R and 2R stand, respectively, for the first and second derivatives of the interatomic distance with respect of the field strength. All quantities are expressed in au except the interatomic distances in Å and the frequencies in cm\(^{-1}\).

### Maximum of \( k_e \) search

<table>
<thead>
<tr>
<th>( F_e^{\pm} )</th>
<th>( R_e )</th>
<th>( k_e )</th>
<th>( \nu_e )</th>
<th>FS</th>
<th>GS</th>
<th>1S</th>
<th>2S</th>
<th>( F_e^{\pm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00000</td>
<td>1.22016</td>
<td>0.43201</td>
<td>2486</td>
<td>0.83770</td>
<td>-3.32009</td>
<td>4.15780</td>
<td>-115.88604</td>
<td>0.0359</td>
</tr>
<tr>
<td>0.0359</td>
<td>1.19117</td>
<td>0.51560</td>
<td>2716</td>
<td>0.00879</td>
<td>-0.51234</td>
<td>0.52113</td>
<td>-117.90282</td>
<td>0.0403</td>
</tr>
<tr>
<td>0.0403</td>
<td>1.19064</td>
<td>0.51669</td>
<td>2719</td>
<td>-0.13313</td>
<td>-0.09252</td>
<td>-0.04061</td>
<td>-138.92461</td>
<td>0.0400</td>
</tr>
<tr>
<td>0.0400</td>
<td>1.19065</td>
<td>0.51669</td>
<td>2719</td>
<td>-0.12261</td>
<td>-0.12342</td>
<td>0.00081</td>
<td>-137.19724</td>
<td>0.0400</td>
</tr>
</tbody>
</table>

### Minimum of \( R_e \) search

<table>
<thead>
<tr>
<th>( F_e^{\pm} )</th>
<th>( R_e )</th>
<th>1R</th>
<th>2R</th>
<th>( F_e^{\pm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00000</td>
<td>1.22016</td>
<td>-2.04075</td>
<td>73.35508</td>
<td>0.0278</td>
</tr>
<tr>
<td>0.0278</td>
<td>1.19391</td>
<td>-0.62463</td>
<td>41.63841</td>
<td>0.0428</td>
</tr>
<tr>
<td>0.0428</td>
<td>1.19068</td>
<td>0.09474</td>
<td>60.40975</td>
<td>0.0412</td>
</tr>
<tr>
<td>0.0412</td>
<td>1.19062</td>
<td>0.00132</td>
<td>56.46291</td>
<td>0.0412</td>
</tr>
</tbody>
</table>

*a* 1S = FS−GS = (d\( k_e \)/d\( F_e \))\( F_e = F_e^{\pm} \); 2S = (d\(^2\)\( k_e \)/d\( F_e^2 \))\( F_e = F_e^{\pm} \); 1R = (d\( R_e \)/d\( F_e \))\( F_e = F_e^{\pm} \); 2R = (d\(^2\)\( R_e \)/d\( F_e^2 \))\( F_e = F_e^{\pm} \).
Table 3. Evolution of different molecular parameters in the Newton–Raphson search of the maximum of the force constant \(k_e\) and the minimum of the interatomic distance \(R_e\) with the electric field strength \(F_e\) for the HLi molecule. 1S stands for the first-order Stark effect and 2S the second-order Stark effect; \(\nu_e\) is the harmonic frequency. FS and GS are the first and second terms in equation (11). \(F_e^{\ell+1}\) represents the strength of the field to be applied in the next search step. 1R and 2R stand, respectively, for the first and second derivatives of the interatomic distance with respect of the field strength. All quantities are expressed in au except the interatomic distances in Å and the frequencies in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>(F_e)</th>
<th>(R_e)</th>
<th>(k_e)</th>
<th>(\nu_e)</th>
<th>FS</th>
<th>GS</th>
<th>1S</th>
<th>2S</th>
<th>(F_e^{\ell+1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>1.60562</td>
<td>0.13655</td>
<td>1431</td>
<td>-0.3184</td>
<td>1.7792</td>
<td>-2.0976</td>
<td>-72.4306</td>
<td>-0.0290</td>
</tr>
<tr>
<td>-0.0290</td>
<td>1.70748</td>
<td>0.06678</td>
<td>1001</td>
<td>2.22864</td>
<td>-16.6843</td>
<td>18.91296</td>
<td>-304.37543</td>
<td>-0.0228</td>
</tr>
<tr>
<td>-0.0228</td>
<td>1.57177</td>
<td>0.14784</td>
<td>1489</td>
<td>3.35677</td>
<td>-2.59285</td>
<td>5.94961</td>
<td>-347.51034</td>
<td>-0.0211</td>
</tr>
<tr>
<td>-0.0211</td>
<td>1.56689</td>
<td>0.15429</td>
<td>1521</td>
<td>1.40575</td>
<td>-0.89962</td>
<td>2.30537</td>
<td>-1161.27467</td>
<td>-0.0191</td>
</tr>
<tr>
<td>-0.0191</td>
<td>1.56517</td>
<td>0.15721</td>
<td>1535</td>
<td>0.70160</td>
<td>-0.13650</td>
<td>0.83810</td>
<td>-479.29492</td>
<td>-0.0174</td>
</tr>
<tr>
<td>-0.0174</td>
<td>1.56537</td>
<td>0.15804</td>
<td>1539</td>
<td>0.42797</td>
<td>0.24383</td>
<td>0.18414</td>
<td>-313.36895</td>
<td>-0.0168</td>
</tr>
<tr>
<td>-0.0168</td>
<td>1.56570</td>
<td>0.15810</td>
<td>1540</td>
<td>0.35745</td>
<td>0.35064</td>
<td>0.00681</td>
<td>-279.02044</td>
<td>-0.0168</td>
</tr>
</tbody>
</table>

Table 4. Evolution of different molecular parameters in the Newton–Raphson search of the maximum of the force constant \(k_e\) and the minimum of the interatomic distance \(R_e\) with the electric field strength \(F_e\) for the CO molecule. 1S stands for the first-order Stark effect and 2S the second-order Stark effect; \(\nu_e\) is the harmonic frequency. FS and GS are the first and second terms in equation (11). \(F_e^{\ell+1}\) represents the strength of the field to be applied in the next search step. 1R and 2R stand, respectively, for the first and second derivatives of the interatomic distance with respect of the field strength. All quantities are expressed in au except the interatomic distances in Å and the frequencies in cm\(^{-1}\).

<table>
<thead>
<tr>
<th>(F_e)</th>
<th>(R_e)</th>
<th>(1R)</th>
<th>(2R)</th>
<th>(F_e^{\ell+1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.0185</td>
<td>1.56510</td>
<td>0.03446</td>
<td>572.08818</td>
<td>-0.0186</td>
</tr>
<tr>
<td>-0.0186</td>
<td>1.56510</td>
<td>-0.02338</td>
<td>584.81931</td>
<td>-0.0186</td>
</tr>
</tbody>
</table>

The internuclear distance with respect to the field. In order to locate these points the only equations required are (5), (6), and (11). Another possibility for calculating the maximum of the force constant would have been choosing equation (9) and proceeding in a way analogous to equation (6). In this case we would have calculated the maximum of the harmonic frequency which, in fact, coincides with the maximum of the force constant (equation (8a)). As a consequence of the use of the force constant expansion instead of the frequency expansion, what we call the Stark effect is not actually the classical Stark effect reported in the literature (equation (1)). The conversion between these parameters is given by equation (8a). Taking \(k_e\) and the first derivative of \(k_e\) in au, and \(\nu_e\) in cm\(^{-1}\), expression (8a) has to be divided by the value 5.14218 \times 10^5, which is the conversion factor from atomic units of electric field strength to V cm\(^{-1}\), to obtain the Stark effect in the most common units.
for instance, in the case of zero field, values for the Stark effect are $-9.85 \times 10^{-7}$, $23.3 \times 10^{-7}$, $-21.4 \times 10^{-7}$ and $6.23 \times 10^{-7}$ in cm$^{-1}$ V$^{-1}$ cm$^{-1}$, respectively, for HF, BH, HLI, and CO.

The frequency maxima of the HF, BH and HLI molecules lie in the same sign region of the electric field as predicted in [20]. In a strict way, this position depends on the sign of the first-order Stark effect at zero field, and thus it is a function of some molecular parameters which are difficult to predict a priori for a given molecule. However, if we consider that the maximum of the force constant and the minimum of the interatomic distance both lie in the same field sign region, which is one of the consequences of Hermansson’s approximation, the field sign at the frequency maximum also can be predicted by the $a_{11}$ sign at zero field (equation (5)). It is worth noting that in the four cases studied the Stark effect (first derivative of $k_e$) signs at zero field coincide with the field signs at the maximum of $k_e$, and are opposite to those of the first derivative of the equilibrium interatomic distance at zero field. Function curvatures for the plots of the force constant versus field agree with those presented in [20], e.g., for the case of the HLI molecule, where the curve is very sharp compared with those of the other species (large value of the second-order Stark effect).

Table 5 presents the values of the field strength at the maximum of $k_e$ and the minimum of $R_e$ curves for every molecule studied. In the same table the respective values obtained by Hermansson and Tepper [20] are listed. Here we must note that these authors worked at the MP4 level with large basis sets and that, as it has been shown [21], parameters $a_{ij}$ have a basis set and level of calculation dependence which in some cases can be important. Therefore, only trends followed by these numbers are actually comparable.

It is interesting also to comment on the sign of the electric field strength where the critical points are achieved. In particular, only two molecules reach the maximum of the force constant under positive fields. In the electric field convention that we have chosen (figure 1) this corresponds to stable situations because the field has a sign opposite to the molecular dipole moment. One way to confirm this situation is by looking at the so-called pseudorotations [6–9], i.e., the two rotations about axes perpendicular to the field direction appearing in the frequency analysis; those frequencies are nonzero when an external perturbation is present.

If the force constants associated to these two pseudorotations are positive (real frequencies), the molecule is in a stable situation with respect to the field, while a negative force constant (imaginary frequency) means that the molecule has a tendency to rotate in order to acquire the most stable orientation. In the species studied, the analysis of pseudorotations confirms the predictions of the stability made from the electric field polarity with respect to the dipole moment at zero field.

The most direct conclusion from this analysis is that the maximum of the force constant can be detected experimentally only in the case of the BH and CO molecules. The same arguments are valid for the minimum of the interatomic distance, where the same two molecules can, in theory, reach this point.

Table 5 reveals that maxima of HF, BH and HLI follow the same trends as given in [20]. The relative coincidence of the results in the case of the HLI molecule can be attributed to the fact that, due to the size of this system, correlation effects are less important. On this particular question we can conclude that the level of calculation does affect the position of the maximum to a large extent. It is also worth noting the close proximity of the two critical points ($k_{\text{max}}(F)$ and $R_{\text{min}}(F)$). The largest separation between these points is about 0.01 au of electric field strength in the case of the HF molecule. The near coincidence of these two critical points is due to the relationship between the force constant and the equilibrium distance. In principle, a large force constant corresponds to a small interatomic distance. However, the two points would coincide if the only effect of the field were geometric (second term RHS in equation (12) or RHS term in equation (11)), but there is also the effect of the electric field on the electronic cloud, which will also modify the force constant (first term RHS in equation (12) or LHS term in equation (11)).

### Table 5. Field strengths (in au) at the maximum of the force constant ($k_e$) and the minimum of the interatomic distance ($R_e$) curves for the different molecules studied. The column HT contains the results from [20]. 1 au$F$ = 5.1421 x 10$^9$ V cm$^{-1}$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Property</th>
<th>HT</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>FH</td>
<td>$k_{\text{max}}$</td>
<td>-0.039</td>
<td>-0.0521</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{min}}$</td>
<td>-0.048</td>
<td>-0.0630</td>
</tr>
<tr>
<td>BH</td>
<td>$k_{\text{max}}$</td>
<td>0.036</td>
<td>0.0400</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{min}}$</td>
<td>0.026</td>
<td>0.0412</td>
</tr>
<tr>
<td>HLI</td>
<td>$k_{\text{max}}$</td>
<td>-0.012</td>
<td>-0.0168</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{min}}$</td>
<td>-0.014</td>
<td>-0.0186</td>
</tr>
<tr>
<td>CO</td>
<td>$k_{\text{max}}$</td>
<td>—</td>
<td>0.0852</td>
</tr>
<tr>
<td></td>
<td>$R_{\text{min}}$</td>
<td>—</td>
<td>0.0948</td>
</tr>
</tbody>
</table>

5. Conclusion

In the formulation of the vibrational Stark effect obtained from the expansion in power series of the potential energy of a molecule in the presence of an electric field, we have found the expressions for the first- and second-order Stark effects together with the
first and second derivatives of the interatomic distance with respect to the electric field strength for a diatomic molecule. A novel approach has been proposed involving the reexpansion of the energy about different field-optimized geometries. This approach, which brings about no truncation of the expansions, requires only the calculation of a few low order energy derivatives. The expressions derived have been used to find the maximum of the frequency versus field curve and the minimum of the interatomic distance versus field curve for four selected diatomic molecules. The expression determined for the first-order Stark effect corrects that found in the literature, which is found to be incomplete. The experimental location of the critical points studied seems to be difficult in some cases, when they are found for field strength values making the molecule unstable to rotation.

We thank Professor Bernard Kirtman for many helpful comments. Financial help has been provided by the ‘Dirección General de Investigación Científica y Técnica’ under Contract PB95-0333.

References
[21] Luis, J. M., Martí, J., Duran, M., and Andrés, J. L., 1995, J. chem. Phys., 102, 7573; the vibrational contribution formulae for α and β in this reference are only approximate; for diatomics, these formulae are complete in [22].