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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, 17017 Girona, Catalonia, Spain

Running title

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Corresponding author

Josep Martí

Institut de Química Computacional

Campus de Montilivi

Universitat de Girona

17071 Girona, Catalonia, Spain.

Abstract

The behavior of the harmonic infrared frequency of diatomic molecules submitted to the influence of moderate static uniform electric fields is analyzed. For this purpose, we have used the development of the potential energy expression 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 function expressions obtained, which correspond to the first- and second-order Stark effects, we are able to find the maxima of the frequency vs. field strength curve for a series of molecules using a Newton-Raphson search. For that purpose we propose to use a method which requires only the calculation of a few energy derivatives at a particular value of the field strength. At the same time, the expression of the dependence of the interatomic distance on the electric field strength is also derived and the minimum of this curve is found for the same species. Derived expressions and numerical results are compared and discussed with previous works found in the literature.

Introduction

The vibrational Stark Effect (VSE) has become an important subject of study in the field of heterogeneous catalysis and surface chemistry. The behavior of the vibrational spectra of species chemisorbed on certain metallic surfaces or in other materials like zeolites can be partially explained 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]. Experimental evaluation of these parameters has also been carried out by several authors using special spectroscopic techniques[11-16].

There are two main parameters related with the experimental study of the VSE: the Stark tuning rate ($\delta_{\nu E}$), and the Infrared cross section change (δ_{SE}). The first one ($\delta_{\nu E}$) represents the rate change of the position of the infrared bands with the electric field strength, while the second one (δ_{SE}) is the rate change of the intensity of the infrared bands with the electric field strength.

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

$$\delta_{\nu E} = \left(\frac{d\nu}{dF} \right)_{F=0} \quad (1)$$

Knowledge of this parameter allows to 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 only valid for low values of the field strength and that the behavior of the frequency vs. field strength curve is not linear in 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 trend 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 considering various interacting species (water, different metallic cations, and a uniform electric field). In spite of the fact that the electric fields involved in the chemical bond are far from being uniform, even for weak bonds, frequency up- and downshifts are found depending on the molecular interaction strength. Thus, this author[17] performed ab initio calculations of the frequency vs. 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 (between 0.01 and 0.1 au of field strength). In later papers, Hermansson[18-20] tried also to establish a correlation between the behavior of 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.

In the last years our group has developed a methodology for the study of the vibrational contributions to the electrical properties which allows to obtain compact expressions for these contributions[21-23]. This formulation can be also used 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 in 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 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 thus to use the methodology developed in refs. 21 and 22 to analyze 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 vs. field curve. In a similar way, condition for the minimum of the internuclear distance vs. field curve will be studied in order to compare the nature of

these two singular points. Moreover, we try to limit the effort of calculating high-order energy derivatives, thus allowing for fast and accurate determination of maxima of v_e .

In the methodological section, the basic theory related to the interaction of a uniform electric field with a diatomic molecule will be outlined, and expressions connected with the Stark effect will be extracted from this theory. In the results section, we will take four selected diatomic molecules in order to apply the developed formulation.

Methodology

The energy of a molecule submitted to the effect of a uniform electric field can be expressed by the following expansion:

$$V = V_0 - \sum_i^{x,y,z} \mu_i F_i - \frac{1}{2!} \sum_{i,j}^{x,y,z} \alpha_{ij} F_i F_j - \frac{1}{3!} \sum_{i,j,k}^{x,y,z} \beta_{ijk} F_i F_j F_k - \dots \quad (2)$$

where F_i represents the component of the static, uniform electric field applied along the i co-ordinate axis, and the coefficients μ , α , β 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:

$$\begin{aligned} V(Q, F) = & a_{00} + a_{10}Q + a_{20}Q^2 + a_{30}Q^3 + a_{40}Q^4 + \dots \\ & + (a_{01} + a_{11}Q + a_{21}Q^2 + a_{31}Q^3)F + \dots \\ & + (a_{02} + a_{12}Q + a_{22}Q^2)F^2 + \dots \\ & + (a_{03} + a_{13}Q)F^3 + \dots \\ & + a_{04}F^4 + \dots \end{aligned} \quad (3)$$

where F stands for the electric field strength, Q is the displacement of the stretching normal co-ordinate from its field-free equilibrium position, and the a_{ij} coefficients are the derivatives of the energy with respect to the coordinate displacement and to the electric field strength. These coefficients respond to the following notation:

$$a_{ij} = \frac{1}{i!j!} \left(\frac{\partial^{(i+j)} V}{\partial Q^i \partial F^j} \right)_{Q=0, F=0} \quad (4)$$

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

Applying the equilibrium condition $\left(\frac{\partial \mathcal{V}}{\partial Q} \right)_F = 0$ to equation 3, one can find the expression of the equilibrium internuclear distance with the field strength, which, to second order in the field strength happens to be:

$$Q_{eq}(F) = -\frac{a_{11}}{2a_{20}} F - \left(\frac{a_{12}}{2a_{20}} - \frac{a_{11}a_{21}}{2a_{20}^2} + \frac{3a_{30}a_{11}^2}{8a_{20}^3} \right) F^2 + \dots \quad (5)$$

Where a_{10} has been set to zero because the expansion is performed at the optimized interatomic distance. Substitution of $Q_{eq}(F)$ in the general potential expansion 3 yields the expression of the equilibrium geometry of the molecule with respect to the field strength. This new 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_{0j} coefficients), 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).

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

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 ν_e by simply recalling the relation between this parameter and the force constant k_e :

$$\nu_e = \frac{1}{2\pi} \sqrt{\frac{k_e}{\mu}} \quad (7)$$

where μ stands for the reduced mass of the system. From this last expression, it is possible to obtain the successive derivatives of ν_e from the derivatives of k_e . In particular, the first and second derivatives of ν_e read:

$$\frac{d\nu_e}{dF} = \frac{\nu_e}{2k_e} \frac{dk_e}{dF} \quad (8a)$$

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

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

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

where ν_e^0 and k_e^0 stand respectively for the harmonic frequency and the force constant in 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 second-order Stark effect.

A point worth being remarked is that all this methodology is based on the assumption that the definition of the force constant is harmonic. Previous calculations of the vibrational Stark effect found in the literature[15] which take into account the anharmonicity, demonstrate that differences with the harmonic approximation are negligible, at least, in the level of approximation where we work. Even though the force constant definition is not anharmonic, the methodology does include anharmonicity in the potential energy through expression 3. This anharmonicity is represented by the a_{30} and a_{40} terms (mechanical anharmonicity) and the a_{ij} terms with $i > 1$ and $j \neq 0$ (electrical anharmonicity).

In order to calculate the maximum of the $k=k(F)$ curve one can indeed make use of eq. 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 this paper we propose a slightly different, yet mathematically equivalent, approach. If one generalizes the potential energy expansion 3 considering as the equilibrium geometry not that of $F_e=0$, but that of a given 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:

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

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 the 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 better account for these changes, the new coefficients will be labeled as a_{ij}^e . Given that all the theory developed for the case $F=0$ (eqs. 5-9) is

still valid for the general case, the condition for the k curve to have a maximum, i.e.,

$\frac{dk}{dF} = 0$, can be written:

$$2a_{21}^e = \frac{3a_{11}^e a_{30}^e}{a_{20}^e} \quad (11)$$

Knowledge of the first and second derivative values of the k_e vs. field strength curve at any field strength value 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 vs. F curve is not the same as that proposed in references 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: $a_{11}^e = 0$. Differences with Hermansson's paper[19] may be due to his misleading 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 at a constant field. This can be mathematically expressed as follows:

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

In the notation proposed, the first partial derivative in equation 12 corresponds to the term $2a_{21}^e$, 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 $6a_{30}^e$ 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 vs. field strength can be determined in a way similar to that of the maximum of the force constant. Indeed, one can make use of eq. 5, and truncate the polynomial properly. However, one can make use of the same technique as done 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 non-zero 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 vs. field curve. This condition can be checked in table 4 of reference 20, where the field strengths that make the dipole moment derivative equal to zero are in general closer to the minimum of the bond length vs. 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.

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 from 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 $< 10^{-6}$ Hartree/Bohr). 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 $a_{20}^e, a_{11}^e, a_{12}^e$ and a_{03}^e with respect to normal coordinates yields

$a_{30}^e, a_{21}^e, a_{22}^e$ 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.

Results and discussion

The theory developed in the preceding section has been applied to 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 been not the case of CO molecule where, as it 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, like in the experimental situation; furthermore, $\frac{d\mu}{dR}$ is quite well reproduced at the Hartree-Fock level. In figure 1, orientations with respect to the electric field vector of the different species studied are outlined, together with the sign convention used for the field.

Figure 1

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, this is, 0.0001 atomic units.

Tables 1-4

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 methodological section (Equation 12). It is important to remark that in the present work we are only interested in the study of the maximum of the force constant and the minimum of the internuclear distance with respect to the field. In order to locate these points the only required equations are Eqs. 5, 6, and 11. Another possibility to calculate 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 (first order Stark effect) is given by equation 8a. Taking k_e and the first derivative of k_e in atomic units, and ν_e in cm^{-1} , the expression has to be divided by the value $5.14218 \cdot 10^9$, which is the conversion factor from atomic units of electric field strength to V/cm, to obtain the Stark effect in the most common units $\text{cm}^{-1}/(\text{V/cm})$. For instance, in the case of zero field, values for the Stark effect are $-9.85 \cdot 10^{-7}$, $23.3 \cdot 10^{-7}$, $-21.4 \cdot 10^{-7}$ and $6.23 \cdot 10^{-7}$ in $\text{cm}^{-1}/(\text{V/cm})$ respectively for HF, BH, HLi, and CO.

Frequency maxima of the HF, BH and HLi molecules lie in the same sign region of electric field as predicted by HT[20]. This position depends on the value 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. Function curvatures for the plots of the force constant vs. field agree also with those presented by HT[20], e.g., for the case of the HLi molecule, where the curve is very sharp compared to those of the other species (large value of the second order Stark effect).

In table 5, we report 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 already shown[21], a_{ij} parameters 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 also interesting 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 at 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 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 the 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 only be detected experimentally 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 V

Table V reveals that maxima of HF, BH and HLi follow the same trends as in the HT work[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. In 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 ($k_{max}(F)$ and $R_{min}(F)$). The largest separation between these points is ca. 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 r.h.s in Eq. 12 or r.h.s. term in Eq. 11), but there is also the effect of the electric field on the electronic cloud, which will also modify the force constant (first term r.h.s in Eq. 12 or l.h.s term in Eq. 11).

Conclusions

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 of 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, yet bringing about no truncation of the expansions, requires only the calculation of a few low-order energy derivatives. The derived expressions have been used to find the maximum of the frequency vs. field curve and the minimum of the interatomic distance vs. field curve for four selected diatomic molecules. The expression found for the first order Stark effect corrects that found in the literature, which is found to be incomplete. 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.

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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) for the **FH** molecule. 1S stands for the first order Stark effect, 2S represents the second order Stark effect, whereas ν_e is the harmonic frequency. FS and GS are the first and second terms in eq. 11. NR 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

F	R_e	k_e	ν_e	FS	GS	1S	2S	NR
0.0000	0.89758	1.45116	4476	-0.25376	3.02958	-3.28334	-53.70927	-0.0611
-0.0611	0.88819	1.53856	4609	0.85055	0.11579	0.73476	-86.20110	-0.0526
-0.0526	0.88847	1.54180	4614	0.64486	0.60695	0.03791	-78.07295	-0.0521
-0.0521	0.88850	1.54181	4614	0.63348	0.63451	-0.00102	-77.64974	-0.0521

Minimum of R_e search

F	R_e	1R	2R	NR
0.0000	0.89758	-0.38528	-5.96060	-0.0646
-0.0646	0.88819	0.01189	-7.46315	-0.0630
-0.0630	0.88819	0.00006	-7.32383	-0.0630

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) for the BH molecule. 1S stands for the first order Stark effect, 2S represents the second order Stark effect, whereas ν_e is the harmonic frequency. FS and GS are the first and second terms in eq. 11. NR 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

F	R_e	k_e	ν_e	FS	GS	1S	2S	NR
0.0000	1.22016	0.43201	2486	0.83770	-3.32009	4.15780	-115.88604	0.0359
0.0359	1.19117	0.51560	2716	0.00879	-0.51234	0.52113	-117.90282	0.0403
0.0403	1.19064	0.51669	2719	-0.13313	-0.09252	-0.04061	-138.92461	0.0400
0.0400	1.19065	0.51669	2719	-0.12261	-0.12342	0.00081	-137.19724	0.0400

Minimum of R_e search

F	R_e	1R	2R	NR
0.0000	1.22016	2.04075	-73.35508	0.0278
0.0278	1.19391	0.62463	-41.63841	0.0428
0.0428	1.19068	-0.09474	-60.40975	0.0412
0.0412	1.19062	-0.00132	-56.46291	0.0412

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) for the **HLi** molecule. 1S stands for the first order Stark effect, 2S represents the second order Stark effect, whereas ν_e is the harmonic frequency. FS and GS are the first and second terms in eq. 11. NR 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

F	R_e	k_e	ν_e	FS	GS	1S	2S	NR
0.0000	1.60562	0.13655	1431	-0.31841	1.77922	-2.09763	-72.43060	-0.0290
-0.0290	1.70748	0.06678	1001	2.22864	-16.68431	18.91296	-3048.37543	-0.0228
-0.0228	1.57177	0.14784	1489	3.35677	-2.59285	5.94961	-3475.10324	-0.0211
-0.0211	1.56689	0.15429	1521	1.40575	-0.89962	2.30537	-1161.27467	-0.0191
-0.0191	1.56517	0.15721	1535	0.70160	-0.13650	0.83810	-479.29492	-0.0174
-0.0174	1.56537	0.15804	1539	0.42797	0.24383	0.18414	-313.36895	-0.0168
-0.0168	1.56570	0.15810	1540	0.35745	0.35064	0.00681	-279.02044	-0.0168

Minimum of R_e search

F	R_e	1R	2R	NR
-0.0185	1.56510	-0.03446	-572.08818	-0.0186
-0.0186	1.56510	0.02338	-584.81931	-0.0186

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) for the CO molecule. 1S stands for the first order Stark effect, 2S represents the second order Stark effect, whereas ν_e is the harmonic frequency. FS and GS are the first and second terms in eq. 11. NR 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

F	R_e	k_e	ν_e	FS	GS	1S	2S	NR
0.0010	1.1023	3.0585	2428	0.8512	-7.2213	8.0725	-84.8439	0.0951
0.0951	1.0858	3.4183	2567	-1.4952	0.0339	-1.5291	-176.8805	0.0865
0.0865	1.0860	3.4254	2569	-1.0196	-0.8395	-0.1801	-139.9675	0.0852
0.0852	1.0860	3.4255	2569	-0.9592	-0.9583	-0.0009	-135.8760	0.0852

Minimum of R_e search

F	R_e	k_e	1R	2R	NR
0.0951	1.0858	3.4183	-0.0020	-6.5071	0.0948
0.0948	1.0858	3.4187	0.0000	-6.4540	0.0948

Table 5- Field strengths (in atomic units) at the maximum of the force constant (k_e) and the minimum of the interatomic distance (R_e) curves for the different molecules studied. Results labeled as HT correspond to results in reference 20. $1 \text{ uaF} = 5.14218 \cdot 10^9 \text{ V/cm}$

Molecule	Property	HT	This work
FH	k_{\max}	-0.039	-0.0521
	R_{\min}	-0.048	-0.0630
BH	k_{\max}	0.036	0.0400
	R_{\min}	0.026	0.0412
Hli	k_{\max}	-0.012	-0.0168
	R_{\min}	-0.014	-0.0186
CO	k_{\max}	-	0.0852
	R_{\min}	-	0.0948

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

