Ro-vibrationally averaged dipole moments of linear triatomic molecules

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Abstract

We discuss the vibrationally averaged dipole moments of linear triatomic molecules (i.e., molecules whose equilibrium structure is linear) with CO_2 and HCO^+ as examples. In recent publications (see T. Hirano, U. Nagashima, P. Jensen, J. Mol. Spectrosc., 343 (2018) 54–61, and references therein) we have demonstrated that a linear triatomic molecule will necessarily be observed as being bent on ro-vibrational average. We show in the present work that there is no contradiction between this result and the experimentally derived, vibrationally averaged dipole moment values obtained for linear triatomic molecules. In particular, we explain that – as determined experimentally – all averaged dipole moment components in the vibrational ground state of $\tilde{X}$ $^1\Sigma$ CO_2 vanish even though the averaged structure of the molecule is bent. This result obviously holds for all symmetrical, linear triatomic molecules of type A–B–A and is caused by the facts that for linear molecules, the rotation about the axis of least moment of inertia (the a axis, which approximately coincides with the molecular axis) cannot be separated from the motion described by variation of the bond angle, and that the dipole-moment function is an odd-function for this rotation. For an unsymmetrical, linear triatomic molecule of type A–B–C, such as HCO^+, the averaged dipole moment component along the a axis is generally non-zero, also in the vibrational ground

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state, and can be determined experimentally, typically by Stark spectroscopy. We calculate the averaged dipole moment component along the a axis to be 3.933 D in the vibrational ground state of $\tilde{X}\ ^1\Sigma^+$ HCO$^+$. This value is in very good agreement with the experimental value, determined from Stark experiments, of 3.921(31) D.

1. Introduction

An experimentally derived value of molecular dipole moment is that measured for ro-vibrating molecule; in most cases it is the value for the ro-vibrational ground state. Ideally, it should be compared to the theoretical counterpart calculated for the corresponding ro-vibrational state. For such calculation, however, we need the ro-vibrational wavefunction and the associated dipole moment function for the state in question, and the ro-vibrational averaging is substantially more complicated than the simple *ab initio* computation of the dipole moment for the equilibrium structure. Consequently, the experimental value of the dipole moment for the ro-vibrational ground state is often compared to the theoretical, *ab initio* dipole moment value calculated at the "equilibrium geometry." The validity of this comparison is not immediately obvious, since the geometry and, hence, the dipole moment value for the relevant ro-vibrational state are more or less different from those for the equilibrium state. Moreover, there is a special feature, as discussed below, in the bending motion of a liner triatomic molecule. Hence, the dipole moment averaged in the molecule-fixed coordinates does not correctly represent the dipole moment value to be observed in the space-fixed laboratory coordinates. Taking these into account, we discuss here theoretically and numerically the ro-vibrationally averaged value of dipole moment of a linear triatomic molecule.

We have discussed previously [1–4] that a "linear" triatomic molecule (i.e., a triatomic molecule with a linear equilibrium structure) will necessarily be observed to be bent on ro-vibrational average. We have verified this assertion theoretically by calculating expectation values of $\bar{\rho}$ (the instantaneous value of the bond angle supplement; $0° \leqslant \bar{\rho} \leqslant 180°$), and experimentally by interpreting experimentally derived rotational constant values [2–4]. The

effective non-linearity is caused by the fact that the bending motion cannot be separated from the rotation about the molecule-fixed axis of least moment of inertia (the a principal axis), which coincides with the molecular axis in the linear equilibrium configuration. Consequently the bending motion is one component of a two-dimensional motion in $(\bar{\rho}, \chi)$. This is one of the two equivalent expressions to describe the doubly degenerate bending vibration of a linear molecule [3].

During the peer-review process of Ref. [4], an anonymous reviewer asked us why the 'permanent' dipole moment (i.e., the vibrationally averaged dipole moment in the vibrational ground state) of the linear molecule CO_2 is experimentally determined to vanish even though, according to our results, the ro-vibrationally averaged structure is slightly bent and therefore a non-zero dipole moment perpendicular to the a axis would be expected. The answer to this question is connected to the fact that as just mentioned, the rotation about the a principal axis cannot be separated from the bending motion (i.e., from the variation of $\bar{\rho}$). When computing a possible permanent dipole moment we must also integrate over an angle (normally called χ; $0° \leqslant \chi < 360°$) describing the rotation about the a axis [3]. The dipole moment components perpendicular to the a axis are odd functions of χ, and so the corresponding integrals – and thus the permanent dipole moment originating in that component – vanish. A permanent dipole moment for a linear triatomic molecule to be observed, therefore, must be oriented along the a axis.

In the present work, we discuss the dipole moment of a linear triatomic molecule, including the issue of the permanent dipole moment vanishing for symmetric molecules of the type CO_2, from a theoretical point of view.

2. Theory, results, and discussion

2.1. Theory

We deal here with an A–B–C "linear" triatomic molecule whose potential energy minimum corresponds to a linear configuration. The geometry of such a molecule is defined by two bond lengths (r_{AB}, r_{CB}) and the bond-angle supplement $\bar{\rho} = 180° - \angle(A–B–C)$ (i.e., the angle measuring the deviation from the linear configuration). Alternatively, we can describe the geometry by the three Jacobi coordinates (r, R, τ) shown in Fig. 1.

Due to the doubly-degenerate nature of the bending motion, the bending wavefunction is that of a two-dimensional oscillator. In a previous paper [3], we have discussed in detail two equivalent expressions for this wavefunction.
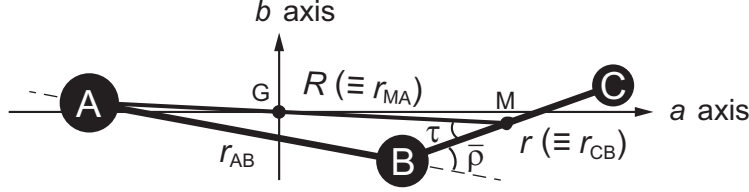
Figure 1: The Jacobi coordinates (r,R,τ) for an A–B–C molecule in the abc principal-axis system. M is the center of mass of the BC moiety, and τ is the angle between the two vectors $\overrightarrow{CB}$ and $\overrightarrow{MA}$. G is the center of mass of the complete molecule. The geometry given for illustration here is drawn to scale for an SCN molecule with $\bar{\rho} = 30°$.

We base the present discussion on the wavefunction expressed in terms of the coordinates $(\bar{\rho}, \chi)$ (see Ref. [3]), where $\bar{\rho}$ is measured in the instantaneous molecular plane defined by the bending motion while χ defines the orientation of this plane in space about the a axis. The potential energy function does not depend on χ and so the molecular plane rotates isotropically around the molecular a axis. See Fig. 1 for the definition of the geometrical variables.

Experimental dipole moment values are normally determined with Stark spectroscopy, that is, by measuring absorption spectra of molecules in external electric fields. Polar molecules will tend to align along the electric field applied, whose direction is described in the space-fixed axis system XYZ.

Theoretical values of the dipole moment function at given molecular geometries defined by $(r_{AB}, r_{BC}, \bar{\rho})$ are calculated as finite-electric-field derivatives of the electronic energy. In the DVR (Discrete Variable Representation) method DVR3D [2, 5], we employ the Jacobi coordinates (r, R, τ) to describe the molecular geometry. Hence, the dipole moment function, originally defined in terms of the coordinates $(r_{AB}, r_{CB}, \bar{\rho})$ is transformed to depend on (r, R, τ). The DVR3D vibrational wavefunction Ψ_{vib} for the (v_1, v_2^ℓ, v_3) state depends on (r, R, τ). That is, we calculate expectation values of the principal-axis components of dipole-moment operator $\hat{\mu}_a(r, R, \tau)$, $\hat{\mu}_b(r, R, \tau)$, and $\hat{\mu}_c(r, R, \tau)$, over the DVR3D wavefunctions to obtain averaged dipole moment values $\langle\mu_a\rangle$, $\langle\mu_b\rangle$, and $\langle\mu_c\rangle$ for the vibrational state in question. Henceforth, for brevity we refer to the principal-axis-system abc as "principal coordinates". Note that abc principal coordinates are molecule-fixed coordinates.

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For each of the principal axes i ($= a$, b, c) we have

$$\langle \mu_i \rangle = \langle \Psi_{\text{vib}}(r, R, \tau) \,|\, \hat{\mu}_i(r, R, \tau) \,|\, \Psi_{\text{vib}}(r, R, \tau) \rangle \tag{1}$$

In the DVR3D program, we chose the Jacobi coordinates r, R, τ, to calculate wavefunction Ψ_{vib}. However, the resultant wavefunction Ψ_{vib} and the geometrical variables r, R, $xcos$ ($\equiv \cos \tau$) to define it are all given in terms of a discreet grid point (j, k, l) $(j, k, l = 1, 2, 3...)$ in such a way as $\Psi_{\text{vib}}(j, k, l)$, $r(j)$, $R(k)$, and $xcos(l)$. Numerical integration of Eq. (1) is carried out, therefore, by

$$\langle \mu_i \rangle = \sum_{j,k,l} \left(|\Psi_{\text{vib}}(j, k, l)|^2 \, \mu_i(r(j), R(k), xcos(l)) \right)$$

$$\Big/ \sum_{j,k,l} |\Psi_{\text{vib}}(j, k, l)|^2 \,. \tag{2}$$

Here, $\mu_i(r(j), R(k), xcos(l))$ is a function to yield i principal-coordinate component of the dipole moment for the Jacobi geometry $(r(j)$, $R(k)$, and $xcos(l))$ associated with the grid point (j, k, l).

The $\langle \mu_i \rangle$ $(i = a, b, c)$ can also be calculated approximately from a given set of ro-vibrationally averaged geometrical parameters $(\langle r \rangle, \langle R \rangle, \langle \tau \rangle)$. The thus calculated $\langle \mu_i \rangle$ value will be referred to as $\langle \mu_i^{\text{ave}} \rangle$ $(i = a, b, c)$ since they are calculated from ro-vibrationally averaged geometry;

$$\langle \mu_i^{\text{ave}} \rangle = \mu_i(\langle r \rangle, \langle R \rangle, \langle \tau \rangle). \tag{3}$$

The molecular dipole moment lies in the instantaneous molecular plane. The a and b axes are in this plane and $\langle \mu_a \rangle$ and $\langle \mu_b \rangle$ are generally non-vanishing, together with $\langle \mu_a^{\text{ave}} \rangle$ and $\langle \mu_b^{\text{ave}} \rangle$. The c axis is perpendicular to the molecular plane and so $\langle \mu_c \rangle = \langle \mu_c^{\text{ave}} \rangle = 0$ for any triatomic molecules.

The vibrationally averaged μ_i $(i = a, b)$ components are approximately given by the dipole moment function computed at the vibrationally averaged structure [Eq. (3)]. Thus, the dipole moment value corresponding to the experimental counterpart is calculated as the expectation value of μ_i or approximately as μ_i^{ave} $(i = a, b)$.

2.2. Correspondence with experimentally derived values of the dipole moment

In computing the non-vanishing, averaged dipole moment components $\langle \mu_a \rangle$ and $\langle \mu_b \rangle$, we have only considered the three vibrational coordinates

$(r,\ R,\ \tau)$ [or, equivalently, $(r_{AB},\ r_{CB},\ \bar{\rho})$]. However, as mentioned above (and explained in detail in Ref. [3]) we cannot separate the bending motion resulting from variation of $\bar{\rho}$ from the rotation of the instantaneous molecular plane about the a axis. This rotation is described by the angle χ [3]. In order to compute molecular absorption or emission intensities, and in order to calculate the energy shifts resulting from the Stark effect, we require matrix elements of the dipole moment components along the the space-fixed axes XYZ, and we must take into account the coordinate χ. For simplicity, we consider here a situation in which the Z axis coincides with the a axis. The X and Y axes are perpendicular to Z and we define the angle χ such that the X and b axes coincide for $\chi = 0$. In this simplified situation, we obtain the space-fixed, vibrationally averaged [over the coordinates $(a,\ b,\ c)$] X, Y, and Z components of the dipole moment as

$$(\mu_X, \mu_Y, \mu_Z) = (\langle \mu_b \rangle \cos \chi, \langle \mu_b \rangle \sin \chi, \langle \mu_a \rangle). \tag{4}$$

In the following discussion, in place of the discrete DVR wavefunction Ψ_{vib} defined in the molecule-fixed coordinates, we will employ a Laguerre-Gauss bending wavefunction $\varphi_{v,\ell}(\bar{\rho}, \chi)$ (Eq. (18) of Ref. [3]),

$$\varphi_{v,\ell}(\bar{\rho}, \chi) = N\, \phi_{v,\ell}(\bar{\rho})\, \exp\left(i\ell\chi\right), \quad (0 \le \bar{\rho} \le \pi,\ 0 \le \chi < 2\pi), \tag{5}$$

which is the bending wavefunction of a linear molecule defined in the space-fixed coordinates. We see in Eq. (5) that the χ-dependence of this wavefunction is described by the normalized factor $\exp(i\ell\chi)/\sqrt{2\pi}$. Averaging the space-fixed dipole moment component μ_A $(A = X, Y, Z)$ over χ, we obtain

$$\langle \mu_A \rangle = \frac{1}{2\pi} \int_0^{2\pi} \exp(-i\ell\chi)\, \mu_A\, \exp(i\ell\chi)\, \mathrm{d}\chi = \frac{1}{2\pi} \int_0^{2\pi} \mu_A\, \mathrm{d}\chi. \tag{6}$$

Inserting the μ_A components from Eq. (4) yields

$$\langle \mu_X \rangle = \frac{1}{2\pi} \langle \mu_b \rangle \int_0^{2\pi} \cos \chi\, \mathrm{d}\chi = 0, \tag{7}$$

$$\langle \mu_Y \rangle = \frac{1}{2\pi} \langle \mu_b \rangle \int_0^{2\pi} \sin \chi\, \mathrm{d}\chi = 0, \tag{8}$$

$$\langle \mu_Z \rangle = \quad \langle \mu_a \rangle. \tag{9}$$

For a linear triatomic molecule the doubly degenerate nature of the bending motion requires us to consider the four vibrational coordinates $(r,\ R,\ \tau,\ \chi)$.

We have now shown that averaging over all four coordinates causes the dipole moment components perpendicular to the molecular axis (μ_X and μ_Y here) to vanish, whereas the component along the molecular axis (μ_Z here) can attain a non-zero value.

When doing Stark spectroscopy and thus applying a constant electric field $\mathbf{E}$, we choose the space-fixed axis system XYZ such that the Z axis is directed along $\mathbf{E}$ whose space-fixed coordinates become $(0, 0, E_Z)$. In this situation, the Stark Hamiltonian is

$$\hat{H}_{\text{Stark}} = \mathbf{E} \cdot \boldsymbol{\mu} = E_Z \, \mu_Z, \tag{10}$$

where $\boldsymbol{\mu}$ is the dipole moment vector, and the first-order Stark shift becomes

$$\Delta E_{\text{Stark}} = \langle \hat{H}_{\text{Stark}} \rangle = E_Z \, \langle \mu_Z \rangle = E_Z \, \langle \mu_a \rangle \tag{11}$$

from Eq. (9). This is also the equation on which we rely when we calculate theoretical dipole moment value as the finite electric-field derivative of *ab initio* calculated energies [6, 7].

Except for ultra-high speed molecular spectroscopy, the time scale of the rotation of the instantaneous bending plane about the a axis is much faster than that of the experimental dipole moment measurement, and hence the b components will be averaged out to zero value due to the internal rotation about a axis, so that the direction of dipole moment vector effectively coincides with the molecular a axis.

Therefore, in a Stark spectroscopy experiment, polar molecules (with a non-zero permanent dipole moment along the molecular axis, $\langle \mu_a \rangle \approx \langle \mu_Z \rangle \neq 0$) will align to a considerable extent along $\mathbf{E}$, so that the molecular a axis will be nearly collinear with the space-fixed Z axis and Eq. (11) will be approximately valid. That is, from the measured Stark shifts we can derive a value of $\langle \mu_a \rangle$, the vibrationally averaged dipole moment component along the molecular axis.

The vibrationally averaged dipole moment along the b axis, $\langle \mu_b \rangle$, does not influence the first-order Stark shifts. However, it predominantly determines the intensities of the bending fundamental, i.e., the vibrational transition $(v_1, v_2^{\ell_2}, v_3) = (0, 1^1, 0) \leftarrow (0, 0^0, 0)$. When we calculate a transition moment of a vibrational transition involving $\ell_2' \leftarrow \ell_2''$, the integration over χ in Eq. (6)

is replaced by

$$\langle M_A^{(\mathrm{tr})}\rangle = \frac{1}{2\pi}\int_0^{2\pi}\exp(-i\ell_2'\chi)\,\mu_A\,\exp(i\ell_2''\chi)\,\mathrm{d}\chi$$

$$= \frac{1}{2\pi}\int_0^{2\pi}\mu_A\,\exp(-i\Delta\ell_2\chi)\,\mathrm{d}\chi. \tag{12}$$

where $\Delta\ell_2 = \ell_2' - \ell_2''$.

Section 17.5.2 of Ref. [8] discusses the correlation between transitions of linear and bent triatomic molecules. It is shown (in particular, see Fig. 17-7 of Ref. [8]) that the vibrational transition $(v_1, v_2^{\ell_2}, v_3) = (0, 1^1, 0) \leftarrow (0, 0^0, 0)$ correlates with a progression of ro-vibrational transitions with $K_a = 1 \leftarrow 0$ in the vibrational ground state of the bent triatomic molecule, involving varying J values. It follows that the upper and lower states of transitions in the $(v_1, v_2^{\ell_2}, v_3) = (0, 1^1, 0) \leftarrow (0, 0^0, 0)$ vibrational band involve only one vibrational wavefunction ψ_{rv} and, consequently, Eq. (4) is valid also for the vibrational band. We obtain from Eqs. (4) and (12) that Eqs. (7)-(9) are now replaced by ($\Delta\ell_2 = 1$)

$$\langle M_X^{(\mathrm{tr})}\rangle = \frac{1}{2\pi}\,\langle\mu_b\rangle\int_0^{2\pi}\exp(-i\,\chi)\,\cos\chi\,\mathrm{d}\chi = \frac{1}{2}\,\langle\mu_b\rangle, \tag{13}$$

$$\langle M_Y^{(\mathrm{tr})}\rangle = \frac{1}{2\pi}\,\langle\mu_b\rangle\int_0^{2\pi}\exp(-i\,\chi)\,\sin\chi\,\mathrm{d}\chi = -\frac{i}{2}\,\langle\mu_b\rangle, \tag{14}$$

$$\langle M_Z^{(\mathrm{tr})}\rangle = \frac{1}{2\pi}\,\langle\mu_a\rangle\int_0^{2\pi}\exp(-i\,\chi)\,\mathrm{d}\chi = 0 \tag{15}$$

where we have used that $\cos\chi = [e^{i\chi} + e^{-i\chi}]/2$ and $\sin\chi = -i[e^{i\chi} - e^{-i\chi}]/2$. The intensity of the vibrational band $(v_1, v_2^{\ell_2}, v_3) = (0, 1^1, 0) \leftarrow (0, 0^0, 0)$ originates in two non-vanishing vibrational transition moments $\langle M_X^{(\mathrm{tr})}\rangle$ and $\langle M_Y^{(\mathrm{tr})}\rangle$ where $|\langle M_X^{(\mathrm{tr})}\rangle| = |\langle M_Y^{(\mathrm{tr})}\rangle| = |\langle\mu_b\rangle|/2$.

2.3. CO_2

2.3.1. Symmetry predictions

The molecular symmetry group [8, 9] for the CO_2 molecule is (see Table B.15 of Ref. [9])

$$\boldsymbol{D}_{\infty\mathrm{h}}(\mathrm{M}) = \{E, (12), E^*, (12)^*\} \tag{16}$$

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where E is the identity operation, (12) is the interchange of the two O nuclei, E^* is the spatial inversion operation, and $(12)^* = (12)\,E^*$ [8, 9].

Table B.15 of Ref. [9] shows that $\boldsymbol{D}_{\infty h}(M)$ has the four irreducible representations [8, 9] $\Sigma_g{}^+$, $\Sigma_u{}^+$, $\Sigma_g{}^-$, and $\Sigma_u{}^-$, where $\Sigma_g{}^+$ is the totally symmetric representation.

It is easily shown [8, 9] that $\hat{\mu}_a(r, R, \tau)$, the a component of the dipole moment operator, is antisymmetric under (12) and unchanged by E^*. That is, it has $\Sigma_u{}^+$ symmetry in $\boldsymbol{D}_{\infty h}(M)$ (Table B.15 of Ref. [9]). When we now use Eq. (1) to calculate $\langle \mu_a \rangle$ for the vibrational ground state with $(v_1, v_2^{\ell_2}, v_3) = (0, 0^0, 0)$, the vibrational wavefunction $\Psi_{\text{vib}}(r, R, \tau)$ has $\Sigma_g{}^+$ symmetry and the symmetry of the integrand in Eq. (1) is $\Sigma_g{}^+ \otimes \Sigma_u{}^+ \otimes \Sigma_g{}^+ = \Sigma_u{}^+ \neq \Sigma_g{}^+$. The integrand does not contain a totally symmetric component, and so the vanishing integral rule [8, 9] causes the integral to vanish, $\langle \mu_a \rangle = 0$. We also have $\langle \mu_a^{\text{ave}} \rangle = 0$ since the averaged structure $(\langle r \rangle, \langle R \rangle, \langle \tau \rangle)$ used to calculate it has $\langle r_{AB} \rangle = \langle r_{CB} \rangle$.

With $\langle \mu_a \rangle = 0$, Eqs. (7)-(9) show that for CO_2, $\langle \mu_X \rangle = \langle \mu_Y \rangle = \langle \mu_Z \rangle = 0$, in accordance with the experimental observations and against the expectations of the anonymous reviewer of Ref. [4].

2.3.2. Numerical confirmation

For $\tilde{X}\ {}^1\Sigma^+$ CO_2, we have constructed *ab initio* 3D PES at the core-valence, mc-CCSD(T)/[aCV5Z (C, O)] level of theory using the program MOLPRO [10]. Here, mc-CCSD(T) denotes the CCSD(T) calculation over the canonical orbitals obtained at the core-valence MCSCF calculations. The basis sets aCV5Z implies aug-cc-pCV5Z [11, 12]. From the 3D PES, ro-vibrational wave functions are determined by DVR method using DVR3D program by Tennyson and coworkers [5].

The dipole moment was calculated as the finite electric field derivative of the core-valence, mc-CCSD(T) energies, and was transformed to the value in the *abc* principal coordinate system at the given geometry. Using these values, in the modified DVR3D program [2], expectation values of $\langle \mu_i \rangle$ $(i = a, b)$ over DVR3D wavefunction are calculated according to Eq. (2). The $\langle \mu_i^{\text{ave}} \rangle$ $(i = a, b)$ values are separately calculated *ab initio* for the ro-vibrationaly averaged structure (Eq. (3)).

Although the permanent dipole moment is 0 D at equilibrium structure, CO_2 consists of polar C–O bonds. The Mulliken net charges calculated at the the core-valence, mc-CCSD(T)/[aCVTZ (C, O)] are -0.256 on each O and +0.512 on C nuclei.

The PES determined as described above is accurate enough to give, for the $(0,0^0,0)$ state of $^{12}C^{16}O_2$, values of the rotational constant B_0 of 0.39002 cm^{-1} (from the term-value spacing) and 0.39003 cm^{-1} (by the perturbation method) against the experimental value of 0.390218966(203) cm^{-1} [13]. The deviation from the experimental value is only -0.05 and -0.10%, respectively. The equilibrium structure for the atomic configuration O1-C-O2 has r_e(O1–C) $= r_e$(C–O2) $= 1.1603$ Å and $\angle$(O1-C-O2) $= 180.0°$. The potential energy minimum is at the linear configuration, so that CO_2 is a "linear" molecule.

The ro-vibrationally averaged geometry (r_0 structure) of $^{12}C^{16}O_2$ calculated as the expectation values over the DVR3D wavefunction has $\langle r$(O1–C)$\rangle_0$ $= \langle r$(C–O2)$\rangle_0 = 1.1652$ Å and $\langle\angle$(O1-C-O2)$\rangle_0 = 173.27°$, i.e., $\langle\bar{\rho}\rangle_0 = 6.73°$. The r_0 structure, derived through the least-squares (LSQ) fitting with $\bar{\rho}$ as a "variable" from the experimentally reported B_0 values [13–15] for six isotopologues, gives r_0(O1–C) $= r_0$(C–O2) $= 1.1650$ Å and $\bar{\rho}_0 = 8.79°$. Thus, theoretically (as expectation value) and experimentally (by LSQ fitting), it is concluded that the ro-vibrationally averaged geometry is observed as being bent.

The question is, then, how about the dipole moment associated with these bent averaged-geometries?

Table 1 shows the calculated dipole moment, expressed in molecule-fixed coordinates, for the various ro-vibrational states of $^{16}O^{12}C^{16}O$, as well as those for the $(0,0^0,0)$ state of the six isotopologues.

In Table 1, the dipole moment value for the $(0,0^0,0)$ state, calculated from the ro-vibrationally averaged geometry ($\langle r$(O1–C)$\rangle_0$, $\langle r$(C–O2)$\rangle_0$, and $\langle\bar{\rho}\rangle_0$) using Eq. (3), is also given. The values obtained lead us to conclude that instead of averaging over the entire wavefunction [Eq. (2)], we can derive acceptably accurate, ro-vibrationally averaged values of the dipole moment directly from the ro-vibrationally averaged geometry [Eq. (3)].

Experimentally we observe the dipole moment in the space-fixed coordinates, and hence, as discussed in the previous section (Section 2.3.1), the b axis component is averaged out to be zero-value through the free-rotation of the molecule about the a axis. The c axis component is always 0 D for any triatomic molecules. The remaining a axis component, which is responsible for the value to be determined by Stark experiment, is shown in Table 1 as being 0 D, as well, for any ro-vibrational states of $^{16}O^{12}C^{16}O$. It means that although the ro-vibrationally averaged structure is observed as being bent, the corresponding dipole moment to be observed in the Stark experi-

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Table 1: Expectation values[a] of dipole moment μ of $\tilde{X}\ ^1\Sigma^+$ CO_2, calculated using Eq. (2) in terms of dipole moment function[b] and DVR3D wavefunction given at each DVR grid point.

$(v_1,v_2^{\ell_2},v_3)$[c]	ν/cm^{-1}	$\langle\bar{\rho}\rangle$/deg.	$\langle\mu_a\rangle$/D	$\langle\mu_b\rangle$/D	$\langle\mu_c\rangle$[d]/D	$\langle\mu_{\mathrm{tot}}\rangle$/D
$^{16}O^{12}C^{16}O$						
μ_e[e]			0.0	0.0	0.0	0.0
$(0,0^0,0)$[f]	0	6.7	0.0000	-0.1634	0.0	0.1634
$(0,1^{1e,f},0)$	670	10.0	0.0000	-0.2413	0.0	0.2413
$(0,2^0,0)$	1288	9.2	0.0000	-0.2239	0.0	0.2239
$(0,2^2,0)$	1341	12.4	0.0000	-0.2997	0.0	0.2997
$(0,3^{1e,f},0)$	1938	11.9	0.0000	-0.2863	0.0	0.2863
$(1,0^0,0)$	2350	6.8	0.0000	-0.1631	0.0	0.1631
$(2,0^0,0)$	4670	6.8	0.0000	-0.1628	0.0	0.1628
$(0,0^0,1)$	1391	9.2	0.0000	-0.2218	0.0	0.2218
$(0,0^0,2)$	2805	12.3	0.0000	-0.2936	0.0	0.2936

Using averaged geometry (Eq. (3))

	$\langle\bar{\rho}\rangle$/deg.	$\langle\mu_a^{\mathrm{ave}}\rangle$/D	$\langle\mu_b^{\mathrm{ave}}\rangle$/D	$\langle\mu_c^{\mathrm{ave}}\rangle$[d]/D	$\langle\mu_{\mathrm{tot}}^{\mathrm{ave}}\rangle$/D
$(0,0^0,0)$ state[f]	6.7	0.0000	-0.1642	0.0	0.1642

Isotopologues

$(0,0^0,0)$ state[f]	$\langle\bar{\rho}\rangle$/deg.	$\langle\mu_a\rangle$/D	$\langle\mu_b\rangle$/D	$\langle\mu_c\rangle$[d]/D	$\langle\mu_{\mathrm{tot}}\rangle$/D
$^{16}O^{12}C^{16}O$	6.7	0.0000	-0.1634	0.0	0.1634
$^{16}O^{13}C^{16}O$	6.6	0.0000	-0.1611	0.0	0.1611
$^{17}O^{12}C^{17}O$	6.7	0.0000	-0.1629	0.0	0.1629
$^{18}O^{12}C^{18}O$	6.7	0.0000	-0.1625	0.0	0.1625
$^{16}O^{12}C^{17}O$	6.7	0.0002	-0.1632	0.0	0.1632
$^{17}O^{12}C^{18}O$	6.7	0.0002	-0.1627	0.0	0.1627
$^{16}O^{12}C^{18}O$	6.7	0.0005	-0.1630	0.0	0.1630

[a] ν: vibrational term value. $\langle\mu_a\rangle$, $\langle\mu_b\rangle$, $\langle\mu_a\rangle$, and $\langle\mu_{\mathrm{tot}}\rangle$ are the expectation values of the a, b, c components, and the total length, respectively, of the dipole moment vector, defined in terms of the abc principal coordinates. A negative value of $\langle\mu_b\rangle$ means that the dipole moment vector is anti-parallel to the b axis (see Fig. 1 for the definition of the abc axes). $\langle\bar{\rho}\rangle$: expectation value of the deviation angle from linearity.
[b] Calculated as the electric field derivative of the core-valence mc-CCSD(T)/[aug-cc-pCV5Z (C, O)] energy at each DVR grid point.
[c] v_1, v_2, and v_3: antisymmetric stretching, bending, and symmetric stretching modes.
[d] The c axis is perpendicular to the instantaneous molecular plane, so the c dipole moment component μ_c = 0 always, and the expectation value $\langle\mu_c\rangle = 0$ (see text).
[e] Dipole moment for the equilibrium structure: $r_\mathrm{e}(O1\text{–}C) = r_\mathrm{e}(C\text{–}O2) = 1.1603$ Å, $\angle_\mathrm{e}(O1\text{–}C\text{–}O2) = 180.0°$.
[f] r_0 structure (DVR3D): $\langle r(O1\text{–}C)\rangle_0 = \langle r(C\text{–}O2)\rangle_0 = 1.1652$ Å, and $\langle\angle(O1\text{–}C\text{–}O2)\rangle_0 = 173.27°$.

ment becomes of zero-value. This result confirms numerically the theoretical prediction that an A-B-A type linear triatomic molecule shows zero dipole-moment even though the ro-vibrationally averaged structure is observed as being bent. This is true for the other A-B-A type isotopologues of CO_2 as shown in Table 1.

For the A-B-A' type, isotopically unsymmetric isotopologues, such as $^{16}O^{12}C^{18}O$, the a axis component $\langle \mu_a \rangle$ of a very small magnitude, of the order of 10^{-4} D, is predicted as shown in Table 1, in accordance of the small difference in ro-vibrationally averaged bond lengths between the two relevant bonds in the molecule. While equilibrium bond lengths are the same for these two bonds, the ro-vibrationally averaged bond lengths differs slightly due to the weight difference in the two terminal atoms: the smaller C–O bond length for the heavier terminal atom. The largest bond-length difference is found in the case of $^{16}O^{12}C^{18}O$ as much as 0.00013 Å. Again, only the $\langle \mu_a \rangle$ component in molecule-fixed coordinate becomes observable in Stark experiments, so that experimentally observable dipole moment value becomes almost of zero-value. The corresponding experimental values are of the order of magnitude similar to the present prediction: 6.05×10^{-4} D for $^{16}O^{12}C^{17}O$ [16], 10^{-3}D [17] and $(7.0 \pm 1.5) \times 10^{-4}$ D [18] for $^{16}O^{12}C^{18}O$. Pure rotational spectroscopy for CO_2 has been carried out utilizing these small dipole moments of isotopologues.

This is the answer to the anonymous reviewer's question, deduced from the numerical results over the ro-vibrational wavefunctions.

2.4. HCO$^+$

2.4.1. Calculation of the potential energy surface and the DVR3D dipole moment function

HCO$^+$ is a classical molecule in molecular spectroscopy. The first reprots in 1970 [19, 20] (in which the molecule was called X-ogen) were followed by many experimental and theoretical publications including those by Neese et al. [21] and by Mladenović and Schmatz [22]. For the other references, the reader is referred to these two papers.

We have constructed a highly accurate *ab initio* 3D potential energy surface (PES) at the core-valence CCSD(T)/[aV5Z (H), aCV5Z (C, O)] level of theory using the MOLPRO [10] program. The basis set aV5Z for H implies aug-cc-pV5Z [23], and aCV5Z for C and O implies aug-cc-pCV5Z [11, 12]. Since HCO$^+$ is a cation, mass-centered coordinates are adopted in the PES

calculations to ensure the correctness of the dipole moment calculation. Using the 3D PES thus determined, the wavefunction at each geometry-grid point is calculated by the DVR3D program developed by Tennyson and co-workers [5].

The dipole moment is calculated as the finite electric field derivative of the core-valence CCSD(T) energy and transformed to the *abc* principal axis components at the given geometry. Then, using modified DVR3D program [2], expectation values of $\langle \mu_i \rangle$ $(i = a, b)$ over DVR3D wavefunction are calculated according to Eq. (2). The average $\langle \mu_c \rangle$ always vanishes since the c axis is perpendicular to the instantaneous molecular plane. The $\langle \mu_i^{\mathrm{ave}} \rangle$ $(i = a, b)$ values are separately calculated *ab initio* for the ro-vibrationaly averaged structure (Eq. (3)). The Mulliken net charges calculated at the core-valence CCSD(T)/[aug-cc-pVTZ (H), aug-cc-pCVTZ (C, O)] level of theory are $+0.828$ (H), $+0.206$ (C), and -0.034 (O), respectively.

The PES has potential energy minimum at the linear configuration, so that HCO^+ is a "linear" molecule, but ro-vibrationally averaged structure over DVR3D wavefunction is calculated as being bent: the r_0 structure has $\langle r(\mathrm{H\text{–}C}) \rangle_0 = 1.1121$ Å, $\langle r(\mathrm{C\text{–}O}) \rangle_0 = 1.1103$ Å, and $\langle \bar{\rho} \rangle_0 = 11.0°$.

The accuracy of the PES is checked by comparing the expectation value of the rotational constant 44594.55 MHz, computed from the term value spacing, for the vibrational ground state of $H^{12}C^{16}O$ with the experimentally reported rotational constant values of 44594.42838(57) MHz [21] and 44594.42880(56) MHz [24]. From these experimental values, the theoretical rotational-constant value deviates by only 0.0003%. Thus, the PES determined here should reproduce accurately the rotational energy structure of HCO^+, and we expect that quite accurate molecular constants, including the equilibrium geometry, can be derived from this PES and the associated wavefunctions.

2.4.2. Vibrationally averaged values of the dipole moment

The molecular symmetry group [8, 9] for the HCO^+ molecule is (see Table B.14 of Ref. [9])

$$\boldsymbol{C}_{\infty \mathrm{v}}(\mathrm{M}) = \{E, E^*\} \, . \tag{17}$$

This group has the two irreducible representations [8, 9] Σ^+ and Σ^-. Σ^+ is the totally symmetric representation and Σ^- symmetry implies anti-symmetry under E^*.

All vibrational coordinates in the two coordinate sets (r, R, τ) and $(r_{AB}, r_{CB}, \bar{\rho})$ used in the present work are invariant under E^* and so each of them

has Σ^+ symmetry in $\boldsymbol{C}_{\infty v}(\mathrm{M})$. Also, the electronic dipole moment components $\hat{\mu}_a(r, R, \tau)$ and $\hat{\mu}_b(r, R, \tau)$ have Σ^+ symmetry. It follows from the vanishing integral rule [8, 9] that the vibrational averages $\langle \mu_a \rangle$ and $\langle \mu_b \rangle$ can be non-vanishing for HCO^+. The c axis component $\langle \mu_c \rangle = 0$ because the c axis is perpendicular to the instantaneous molecular plane.

For $\tilde{X}$ $^1\Sigma^+$ HCO^+, we calculated the ro-vibrationally averaged dipole moment as the expectation values over the DVR3D wavefunctions by Eq. (2) using the a, b, c components of the dipole moment defined at each DVR grid point. The results are given in Table 2.

The dipole moment for the equilibrium structure μ_e, calculated as finite electric field derivative of the core-valence, CCSD(T) energy, is -3.897 D. The very small difference between this value and $\langle \mu_a \rangle = -3.933$ D for the $(0,0^0,0)$ state (Table 2) lends credibility to the conventional practice of comparing the theoretical value for the equilibrium structure to the experimental value for the $(0,0^0,0)$ state.

The averaged dipole moment values $\langle \mu_a \rangle$, $\langle \mu_b \rangle$, $\langle \mu_c \rangle$, and $\langle \mu_{\mathrm{tot}} \rangle$ $(= \langle |\boldsymbol{\mu}| \rangle)$ calculated from the DVR3D wavefunction [Eq.(2)] for the $(0,0^0,0)$ state of HCO^+ are -3.933, 0.117, 0.0, and 3.935 D, respectively. Note that these are values in the molecule-fixed coordinates.

The corresponding dipole moments values $\langle \mu_a^{\mathrm{ave}} \rangle$, $\langle \mu_b^{\mathrm{ave}} \rangle$, $\langle \mu_c^{\mathrm{ave}} \rangle$, and $\langle \mu_{\mathrm{tot}}^{\mathrm{ave}} \rangle$[1] calculated for the vibrationally averaged structure from Eq. (3) give similar values of -3.935, 0.116, 0.0, and 3.937 D, respectively, for the $(0,0^0,0)$ vibrationally averaged geometry $(\langle r(\mathrm{H–C}) \rangle_0 = 1.1121$ Å, $\langle r(\mathrm{C–O}) \rangle_0 = 1.1103$ Å, and $\langle \angle(\mathrm{H–C–O}) \rangle_0 = 169.02°)$.

There is good agreement between $\langle \mu_i \rangle$ value and $\langle \mu_i^{\mathrm{ave}} \rangle$ for $i = a$, b, and tot. This indicates that once we know the vibrationally averaged, geometrical structure, we can reliably estimate from Eq. (3) the vibrationally averaged dipole moment values without actually averaging the electronic dipole moment functions over the vibrational wavefunction.

Note that both sets of averaged dipole moment values are those calculated as components along the molecule-fixed abc coordinate axes. As discussed in Section 2.2 [see Eqs. (7)–(11)], the dipole moment value to be responsible for the value in Stark-spectroscopy experiments is the $\langle \mu_a \rangle$ value, i.e., the vibrationally averaged component along the molecular axis. In the present

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[1]Computed as the length of the electronic dipole moment vector $|\boldsymbol{\mu}|$ at the averaged geometry $(\langle r \rangle, \langle R \rangle, \langle \tau \rangle)$.

Table 2: Dipole moment expectation values[a] for $\tilde{X}\ ^1\Sigma^+$ HCO^+, calculated with Eq. (2) from the dipole moment functions[b] and the DVR3D wavefunctions given at each DVR grid point.

$(v_1,v_2^{\ell_2},v_3)$[c]	ν/cm^{-1}	$\langle\bar\rho\rangle/\mathrm{deg.}$	$\langle\mu_a\rangle/\mathrm{D}$	$\langle\mu_b\rangle/\mathrm{D}$	$\langle\mu_c\rangle$[d]$/\mathrm{D}$	$\langle\mu_{\mathrm{tot}}\rangle/\mathrm{D}$
μ_e[e]			-3.897	0.0	0.0	3.897
$(0,0^0,0)$[f]	0	11.0	-3.933[g]	0.117	0.0	3.935
$(0,1^{1e,f},0)$	832	16.4	-3.910	0.177	0.0	3.915
$(0,2^0,0)$	1644	19.1	-3.887	0.209	0.0	3.895
$(0,2^2,0)$	1660	20.4	-3.887	0.225	0.0	3.894
$(0,3^{1e,f},0)$	2464	22.4	-3.865	0.249	0.0	3.875
$(1,0^0,0)$	3088	11.0	-4.033	0.129	0.0	4.036
$(2,0^0,0)$	6073	11.1	-4.133	0.140	0.0	4.136
$(0,0^0,1)$	2186	11.0	-3.954	0.121	0.0	3.957
$(0,0^0,2)$	4350	11.1	-3.976	0.125	0.0	3.978

[a] ν: vibrational term value. $\langle\mu_a\rangle$, $\langle\mu_b\rangle$, $\langle\mu_c\rangle$, and $\langle\mu_{\mathrm{tot}}\rangle$ are the expectation values of the a, b, c components, and the total length, respectively, of the dipole moment vector, defined in the principal-axis system abc. A negative value of $\langle\mu_a\rangle$ means that the direction of the dipole moment vector is from O toward H.

[b] Calculated as the electric field derivative of the core-valence CCSD(T)/[aug-cc-pV5Z (H), aug-cc-pCV5Z (C, O)] energy at each DVRD grid point.

[c] v_1, v_2, and v_3: antisymmetric stretching, bending, and symmetric stretching modes.

[d] Any triatomic linear molecules do not have the c axis component of the dipole moment.

[e] Dipole moment for the equilibrium structure: $r_\mathrm{e}(\mathrm{H-C}) = 1.0915$ Å, $r_\mathrm{e}(\mathrm{C-O}) = 1.1057$ Å, $\angle_\mathrm{e}(\mathrm{H-C-O}) = 180.0°$.

[f] r_0 structure (from DVR3D): $\langle r(\mathrm{H-C})\rangle_0 = 1.1121$ Å, $\langle r(\mathrm{C-O})\rangle_0 = 1.1103$ Å, and $\langle\angle(\mathrm{H-C-O})\rangle_0 = 169.02°$.

[f] The experimentally derived (unsigned) dipole moment value is 3.921(31) D, determined from cyclotron frequency polarizability shifts [25].

work, for the $(0,0^0,0)$ state, we obtain the theoretical values $\langle \mu_a \rangle = -3.933$ D and $\langle \mu_a^{\text{ave}} \rangle = -3.935$ D.

Both theoretical values are in good agreement with the (unsigned) experimental dipole moment value of $3.921(31)$ D ([25], quoted uncertainty in terms of the last digit given in parentheses), determined from cyclotron frequency polarizability shifts.

Vibrationally averaged dipole moment values determined from DVR3D wavefunctions for various vibrational states are also given in Table 2. We note once again that the component averages $\langle \mu_i \rangle$ ($i = a$, b, c) in Table 2 are defined in the molecule-fixed principal axis system abc, and that the value to be observed in Stark experiments is the $\langle \mu_a \rangle$ in Table 2.

3. Conclusion

We have previously shown [2–4] that even though the potential energy function of a triatomic molecule has its global minimum at a linear geometry (so that in spectroscopic parlance, the molecule is "linear"), nevertheless its structure will be observed as being bent, both experimentally and theoretically. That is, the averaged bond angle supplement $\langle \bar{\rho} \rangle > 0$.

For a linear molecule, we cannot separate the rotation about the molecule-fixed a axis (which approximately coincides with the molecular axis) described by χ from the bending motion described by $\bar{\rho} = 180° - \angle$(A–B–C), and so χ must be considered as a vibrational coordinate.

As seen from Eqs. (7)-(9), when the dipole moment components along space-fixed axes of a linear molecule are averaged over the coordinate χ, the components perpendicular to the molecular axis vanish, irrespective of the fact that the ro-vibrationally averaged structure of the molecule is bent.

Therefore, of the two non-zero, vibrationally averaged dipole moment components $\langle \mu_a \rangle$ and $\langle \mu_b \rangle$ of a linear molecule (defined in molecule-fixed abc coordinates), only $\langle \mu_a \rangle$ can be determined from Stark-spectroscopy experiments [Eq. (11)]. The average $\langle \mu_b \rangle$ determines the intensities of, for example, the bending fundamental band $(v_1, v_2^{\ell_2}, v_3) = (0, 1^1, 0) \leftarrow (0, 0^0, 0)$ [Eqs. (13)-(15)].

We have demonstrated that for a symmetric, linear triatomic molecule of type A–B–A [with molecular symmetry group $\boldsymbol{D}_{\infty h}(M)$ in Eq. (16)] all three averaged, space-fixed dipole moment vanish, in spite of the fact that the molecule has a bent, ro-vibrationally averaged structure. This explains the experimental results for CO_2, the prime example of this type of molecule.

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For a linear triatomic molecule of type A–B–C [with molecular symmetry group $\boldsymbol{C}_{\infty\mathrm{v}}(\mathrm{M})$ in Eq. (17)], such as $\mathrm{HCO^+}$, the vibrational average $\langle\mu_a\rangle$ can be determined experimentally in Stark-type experiments. In the present work, we have calculated theoretical values of $\langle\mu_a\rangle$ and $\langle\mu_b\rangle$ as expectation values over DVR3D wavefunctions for various vibrational states of $\mathrm{HCO^+}$. The theoretical $\langle\mu_a\rangle$ value determined for the vibrational ground state is in very good agreement with the corresponding experimental value.

Since we know that $\langle\mu_i\rangle$ $(i=a,b,c)$ and the corresponding $\langle\mu_i^{\mathrm{ave}}\rangle$ gives, respectively, of similar value, we can determine, though approximately, $\langle\mu_i\rangle$ from the dipole moment values calculated for the ro-vibrationally averaged structure without taking average for $\langle\mu_i\rangle$ over the ro-vibrational wavefunction. In either way, for a liner triatomic molecule, the value responsible for that in Stark experiment is a axis component, and the b axis component is averaged out to zero-value.

The conventional practice of comparing the theoretical dipole moment value for the equilibrium structure with the experimental value for the ro-vibrational ground state $(0,0^0,0)$ is lent credibility by the results presented here, at least for $\mathrm{HCO^+}$.

Acknowledgment

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