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Linear and bent triatomic molecules are *not* qualitatively different!

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Abstract

I, and other authors, have discussed in several recent publications that “linear” triatomic molecules (defined as having linear equilibrium structures) are necessarily observed as being bent on ro-vibrational average. We have demonstrated this theoretically by calculations of the rotation-vibration expectation values $\langle \bar{\rho} \rangle$, where $\bar{\rho} = \pi - \angle(\text{A-B-C})$ is the bond angle supplement, $\angle(\text{A-B-C})$ being the instantaneous value of the bond angle of the triatomic molecule A-B-C. Direct experimental evidence of bent average structures has been obtained by other authors in Coulomb Explosion Imaging experiments, and indirect evidence from re-interpretation of experimentally derived rotational-constant values. In spite of a rather significant amount of evidence in support of the bent average structures, the idea has been heavily criticized. In the present work I discuss in more detail some of the arguments for the bent average structures put forward in the previous papers, and I hope to correct and clarify some of the misunderstandings leading to the criticisms. Part of the criticism originates in a widespread, but fallacious, belief among spectroscopists that linear and bent chain molecules have qualitatively different energy-level and spectral intensity patterns. This is not true. One can view the linear-molecule energy level and spectral patterns as limiting cases of the bent-molecule ones.

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I. INTRODUCTION

In several recent papers [1–5] I, and other authors, have discussed the energy level patterns and structures of “linear” triatomic molecules, defined as molecules whose potential energy minimum is at a linear configuration. In particular, it was concluded in this work that such molecules will necessarily be observed to be bent on ro-vibrational average. This assertion has been underpinned theoretically by numerous calculations of the expectation values (see Refs. [2–5] and references therein) of the bond angle supplement $\bar{\rho} = \pi - \angle(\text{A-B-C})$, (where $\angle(\text{A-B-C})$ is the instantaneous value of the bond angle of the triatomic molecule A–B–C), and experimentally by interpreting experimentally derived rotational constant values [2, 4].

I emphasize that I discuss here the *structures* of triatomic molecules. Such a structure is defined by the values of $\bar{\rho}$ and of two bond lengths which, in an obvious notation, are denoted r_{AB} and r_{BC} for the molecule A–B–C. The orientation of the molecule in space (defined by the molecular plane for $\bar{\rho} > 0$) is irrelevant for the structure. One might now ask if our structure investigations are purely theoretical conjecture or if some possibility of experimental verification exists. In Refs. [5, 6] simulations of *Coulomb Explosion Imaging* (CEI) experiments (see Refs. [7, 8] and references therein) were carried out; these experiments aim at determining the (thermally averaged) probability distribution of $\bar{\rho}$. Ref. [5] reports simulations of CEI experiments for the linear ion HCO^+ and compares them with the corresponding experimental results. It turned out that in the existing CEI experiment, the observed HCO^+ ions are in very highly excited states with populations probably described by a non-Boltzmann distribution and, consequently, there were problems in simulating the experimental results. One could conclude, however, that the experimental results are consistent with a bent average structure of HCO^+ . Earlier simulations by myself and others of CEI experiments [8] for the slightly bent CH_2^+ ion [6] was very successful since in the corresponding CEI experiments [8], the ions were allowed to equilibrate to a Boltzmann distribution at an absolute temperature of 300 K.

As mentioned in Ref. [5], the ideas developed in Refs. [1–5, 9] have provoked strong, seemingly emotional protests from recognized experimental spectroscopists. Quite recently, such criticisms have been voiced in Ref. [10], a conference abstract.¹ The motivation for the

¹ The “perpetual” webpage of the Japanese conference series “Symposium on Molecular Spectroscopy” is found at <http://regulus.mtrl1.info.hiroshima-cu.ac.jp/~molspec/e-index.html>. From this page, information about the 19th Symposium, held on 26–27 May 2019, can be reached through the link “Past

present work is to discuss in more detail some of the arguments put forward in the previous papers [1–5, 9], in particular in Ref. [5], thereby hopefully correcting and clarifying some of the misunderstandings leading to the criticisms in Ref. [10].

The confusion regarding the average structure of a linear triatomic molecule is chiefly caused by the fact that the bending motion (i.e., the variation of $\bar{\rho}$) cannot be separated from the rotation about the molecule-fixed a axis, which coincides with the molecular axis in the linear equilibrium configuration. Consequently, the inseparable bending-rotation motion is described by the two coordinates $(\bar{\rho}, \chi)$ with $0 \leq \bar{\rho} \leq \pi$ and $0 \leq \chi < 2\pi$. The angle χ defines the orientation of the instantaneous molecular plane in space as the molecule rotates about the a axis.

The fact that linear and bent molecules are traditionally described by different effective Hamiltonians [12] (i.e., the parameterized Hamiltonians used by experimental spectroscopists to fit their measured transition wavenumbers) has caused many spectroscopists to believe that linear and bent (triatomic) molecules are qualitatively different. This is not so. Already in 1998, P. R. Bunker and I argued in Section 17.5.2 of Ref. [12], that there is a gradual, continuous change from the energy level pattern of a strongly bent triatomic molecule like H₂O to that of a linear triatomic molecule like CO₂, and that one can view the linear-molecule energy level pattern as a limiting case of the bent-molecule one (see, in particular, Fig. 17-7 of Ref. [12] and the discussion of it). In this sense, linear and bent triatomic molecules are *not* qualitatively different.

It was already reported in Ref. [5] how T. Amano, one of the authors of Ref. [10] and a proponent of the linear average structure, wrote me in an e-mail that “the bending motion is like a dog wagging its tail. Half of the time the tail is left, half of the time it is right, and on the average it is in the middle, neither left nor right.” I explained the fallacy of this argument already in a private-communication answer to the e-mail and the arguments were repeated in Ref. [5]. Unfortunately, the explanations did not cause the authors of Ref. [10] to change their views in any discernable way, and therefore I continue here the discussion of the wagging-tail molecule and try to explain our ideas of this as pedagogically as I can by means of Fig. 1.

In Fig. 1a, I have depicted two triatomic A–B–C molecules, playing the roles of two dogs meetings” in the left-hand column. The abstract book of the 19th Symposium is found as a pdf file at <http://regulus.mtr11.info.hiroshima-cu.ac.jp/~molspec/2019symposium/data/abstbook.pdf>. Please go to p. 33 of the pdf file to find the abstract of Ref. [10] (in English).

wagging their tails to the left and right, respectively. Now if we were really looking at two dogs, we would do this on the surface of the Earth where the gravitational pull defines the directions “down” and “up”. So all observers of the two dogs would immediately agree on these two directions. The dogs have easily distinguishable front and rear ends, and since we are mostly interested in their tails, we would agree with all observers of the tail-wagging motion that all observations are made from vantage points behind the dog observed. This would mean that all observers agree not only on the directions “down” and “up”, but also on the directions “left” and “right.” Obviously, on the surface of the Earth we can easily pre-define directions “down”, “up”, “left”, and “right” on which to base our discussion of the two dogs and the directions of their tails.

What about the situation in Fig. 1, where we are considering two triatomic molecules instead of two dogs? Well, we consider each of the molecules in the figure to be isolated. Each of them is alone in the Universe. There is no gravitational pull and therefore no pre-defined “down” and “up.” These directions would have to be chosen arbitrarily together with “left” and “right.” So for a dog, or a molecule, alone in the Universe, the statement that “the bending motion is like a dog wagging its tail. Half of the time the tail is left, half of the time it is right, . . .” is meaningless. How can we define the structure of the molecule in the absence of pre-defined directions? It seems natural to me, and to my co-authors of our previous papers [1–5] on this subject, to define the structure in terms of the values of the geometrically defined, structural parameters $(\bar{\rho}, r_{AB}, r_{BC})$ indicated in Fig. 1. These parameters are not defined in terms of any pre-defined directions. When we now rotate the right-hand triatomic molecule in Fig. 1a by π about the r_{AB} bond, we obtain Fig. 1b, and we see that the left-hand and right-hand molecules have identical structures, i.e. the same values of $(\bar{\rho}, r_{AB}, r_{BC})$. The left-hand and right-hand molecules can be brought to cover each other, they are completely identical and we cannot distinguish them. This makes the statement about “a dog wagging its tail” doubly meaningless. The “left-tail” and “right-tail” situations correspond to identical values of r_{AB} , r_{BC} , and $\bar{\rho}$ and the molecule has the same structure in the two situations. We have already introduced the angle χ describing the rotation of the molecule about the a molecule-fixed axis [12] (i.e., the principal molecule-fixed axis of least moment of inertia, which becomes the molecular axis at linear geometries), and we distinguish between the “left-tail” and “right-tail” situations by means of χ . The two situations correspond to χ -values of χ_{left} and χ_{right} , respectively, where $\chi_{\text{right}} = \chi_{\text{left}} +$

π . That is, we describe the molecule as changing from being “left-tail” to being “right-tail” by free rotational motion, not by bending motion (i.e., variation of $\bar{\rho}$).

Proponents of linear average structures seem to like to focus on the situation of the molecule bending ‘through’ the linear geometry with $\angle(A-B-C) = \pi$ or, equivalently, $\bar{\rho} = 0$. They argue that the molecule is just as often moving towards the linear geometry as it is moving away from it, and so, the average geometry must be linear. This is incorrect, the fallacious idea being that we can magically distinguish these ‘towards’ and ‘away from’ situations. In reality, if the molecule is about to bend through the linear situation and passes through a geometry with $\bar{\rho} = 1^\circ$, say, then after having passed through linearity it passes through a geometry where, *again*, $\bar{\rho} = 1^\circ$. As just described, the molecular structures in the two situations can be brought to cover each other and so they are identical. The passage through the linear geometry is accompanied by an instantaneous change of $\chi \rightarrow \chi + \pi$ and an instantaneous reversal of the b and c axes. The a axis remains unchanged and, in order for the abc axis system to remain right-handed, both the b and c axes must be reversed. With these definitions, we obtain $|\langle \mu_b \rangle| \neq 0$ and that the average structure is bent on observation, also for a linear molecule like CO_2 .

I emphasized above that I, and the co-authors of our previous papers [1–5] on the bending motion and the structure of chain molecules, define the structure of a triatomic molecule in terms of the values of the geometrically defined coordinates $(\bar{\rho}, r_{AB}, r_{BC})$ (Fig. 1). This is analogous to the definition of structure for non-planar, more complicated molecules. We consider for a moment a methyl fluoride molecule CH_3F with the three protons labelled 1, 2, 3. The structure of a CH_3F molecule is given by the instantaneous values of the C–F bond length, the three H_i –C bond lengths, the three bond angles $\angle(\text{H}_i\text{–C–F})$, and two dihedral angles θ_{12} and θ_{23} , where θ_{ij} is the angle between the $\text{H}_i\text{–C–F}$ and $\text{H}_j\text{–C–F}$ planes. The third dihedral angle $\theta_{31} = 2\pi - \theta_{12} - \theta_{23}$ and it is therefore redundant. It seems obvious that the nine coordinates defining the structure of a CH_3F molecule are analogous to the coordinates $(\bar{\rho}, r_{AB}, r_{BC})$ used for a triatomic molecule in that all structural parameters are genuinely geometrically defined; their definitions do not depend on pre-defined directions in space or on the instantaneous orientation of the molecule in space. It also seems obvious that if we initially look at an equilibrium-structure, ball-and-stick model of a CH_3F molecule on the surface of the Earth, with the F nucleus pointing upwards, the structure does not change if we turn the ball-and-stick model upside-down so that the

F nucleus points downwards. In his statement about “a dog wagging its tail”, Amano apparently suggests that the “left-tail” and “right-tail” triatomic molecules in Fig. 1 have different structures, since he sees the linear structure as the average of the two, even though the “left-tail” molecule is obtained by rotating the “right-tail” molecule by π about the A–B bond so that the two structures are identical. They are just oriented differently in space which is irrelevant for their structures. It is self-evident that our CH₃F and A–B–C example molecules retain their structure when rotated in space (for example such that they are turned upside-down). In reality, all molecules retain their structures when they are rotated in space with the relative positions of the nuclei kept unchanged. This is no revolutionary idea. It is generally well known and stated clearly, for example, by Sutcliffe and Tennyson [13, 14]: They start by noting that to describe a molecule with N nuclei, $3N$ coordinates are needed. Three of these coordinates, normally chosen as the space-fixed Cartesian coordinates of the center-of-mass, describe translation and the remaining $3N - 3$ coordinates are required to be invariant under translation. Three further coordinates, normally chosen as Euler angles defined in terms of a molecule-fixed axis system, describe rotation and it is required that remaining $3N - 6$ coordinates are invariant under translation and rotation. The instantaneous structure of the molecule is given in terms of these $3N - 6$ coordinates and it is now obvious that translation and rotation do not influence the structure. It appears, however, that Amano considers the triatomic molecule A–B–C to change its structure when it is rotated by π about the A–B bond (Fig. 1). This is clearly an unreasonable idea. Triatomic molecules are not special in this respect, they are just like all other molecules.

As already argued in Ref. [9], the b dipole-moment component of a linear triatomic molecule like CO₂ determines the intensity of the vibrational transition $(v_1, (v_2^{\text{linear}})^{\ell_2}, v_3) = (0, 1^1, 0) \leftarrow (0, 0^0, 0)$ [9]. For a well-bent triatomic molecule such as H₂O, the b -axis dipole-moment component induces transitions with $|\Delta K_a| = 1$ in the purely rotational spectrum.

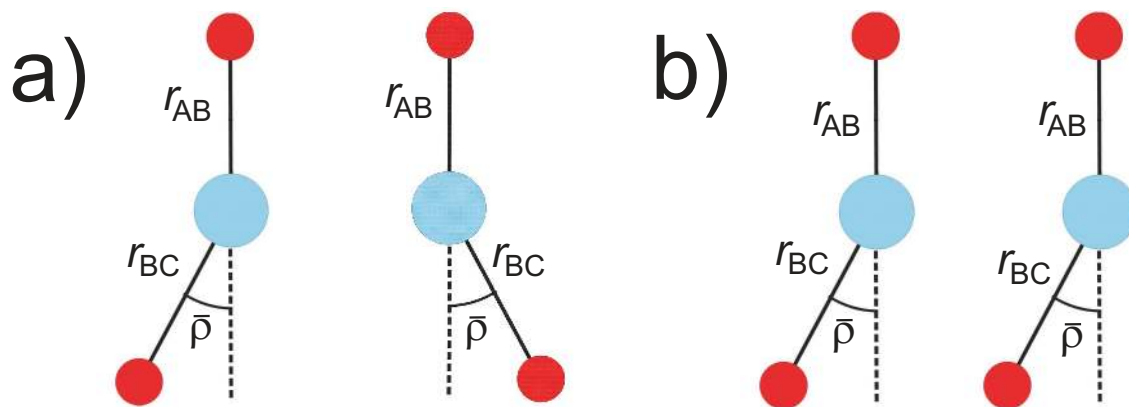


FIG. 1. “Left-tail” and “right-tail” triatomic molecules (see text). Display b) is obtained by rotating the right-hand molecule in display a) by π about the A–B bond. It is seen in display b) that the “left-tail” and “right-tail” molecules are identical; they can be brought to cover each other and have identical values of $(\bar{\rho}, r_{AB}, r_{BC})$.

II. THEORY

A. Rotation-vibration transitions of triatomic molecules

We deal here with a linear molecule of type A–B–C or A–B–A, which has the potential energy minimum at a linear configuration. The rotation-vibration states of a linear triatomic molecule are conventionally labelled by the quantum numbers [12] $(v_1, (v_2^{\text{linear}})^{\ell_2}, v_3, J)$ where v_1 and v_3 are the principal quantum numbers describing the stretching motion, v_2^{linear} is the principal quantum number for the bending motion, ℓ_2 measures the projection of the angular momentum on the molecular a axis, and J is the conventional total-angular-momentum quantum number. Since states with $\ell_2 > 0$ are “doubled”, the two components are distinguished by the labels [11] e and f . The rotation-vibration states of a bent triatomic molecule are conventionally labelled by the quantum numbers [12] $(v_1, v_2^{\text{bent}}, v_3, J_{K_a K_c})$. The correlation between the linear-molecule and bent-molecule labelling is discussed in Section 17.5.2 of Ref. [12] and we obtain

$$K_a = |\ell_2| \quad (1)$$

and

$$v_2^{\text{bent}} = \frac{1}{2} (v_2^{\text{linear}} - K_a). \quad (2)$$

In Ref. [3] (and in the references therein; see also Ref. [12] and references therein) we have

described how the bending motion and the rotation about the a axis cannot be separated and so we have to solve initially the Schrödinger equation for a two-dimensional motion described by the coordinates $(\bar{\rho}, \chi)$. The strategy chosen for this solution is explained in Ref. [3] (see also Chapter 17 of Ref. [12] and references therein). In Ref. [9], we have further discussed the selection rules for absorption/emission transitions between the states with the wavefunctions obtained in Ref. [3]. The intensities of the absorption/emission transitions depend on the molecular dipole moment, and in order to describe this vectorial quantity we introduce a space-fixed axis system [12] XYZ and a molecule-fixed, principal-axis system [12] abc . It is important to appreciate that the abc axis systems follows the rotation of the molecule. The a and b axes are always in the instantaneous molecular plane (defined for $\bar{\rho} > 0$) and so the b axis rotates with this plane as the molecule rotates about the a axis. The instantaneous dipole-moment components μ_a, μ_b in the abc axis system depend solely on the vibrational coordinates $(r_{AB}, r_{BC}, \bar{\rho})$ ($\mu_c = 0$ always because the c axis is perpendicular to the instantaneous molecular plane). For a particular molecular state, for example the ground state, we obtain average dipole-component values $\langle \mu_a \rangle$ and $\langle \mu_b \rangle$ as expectation values over the $(r_{AB}, r_{BC}, \bar{\rho})$ -dependent vibrational wavefunctions. Again, it is important to appreciate that the averages $\langle \mu_a \rangle$ and $\langle \mu_b \rangle$ do not depend on the instantaneous orientation of the molecule in space. That is, they do not depend on the angle χ .

In Ref. [9], we have shown that

- the average $\langle \mu_b \rangle$ gives rise to transitions (in linear-molecule notation) $(v'_1, (v_2^{\text{linear}'})^{\ell'_2}, v'_3, J') \leftarrow (v''_1, (v_2^{\text{linear}''})^{\ell''_2}, v''_3, J'')$ with $|\Delta \ell_2| = |\ell'_2 - \ell''_2| = 1$.
- the average $\langle \mu_a \rangle$ gives rise to transitions with $\Delta \ell_2 = 0$.

It should be noted that in arguing for the values of $|\ell'_2 - \ell''_2| = 0(1)$ for transitions induced by the dipole moment averages $\langle \mu_a \rangle (\langle \mu_b \rangle)$, we considered in Ref. [9], for pedagogical reasons, a simplified situation where the Z and a axes are parallel. The same result is obtained, however, by considering a general situation.

For an A–B–C molecule with the molecular symmetry group $\mathbf{C}_s(\text{M})$ [12] a.k.a. $\mathbf{C}_{\infty v}(\text{M})$ (see below), the averages $\langle \mu_a \rangle$ and $\langle \mu_b \rangle$ will generally be non-vanishing and such a molecule will, in particular, have a rotational spectrum with transitions $(0, 0^0, 0, J'' + 1) \leftarrow (0, 0^0, 0, J'')$. For an A–B–A molecule such as CO_2 with the molecular symmetry group $\mathbf{C}_{2v}(\text{M})$ [12] a.k.a. $\mathbf{D}_{\infty h}(\text{M})$ (see below), $\langle \mu_b \rangle$ is non-vanishing but $\langle \mu_a \rangle = 0$ by symmetry [9] and such a molecule

has *no* rotational spectrum with transitions $(0, 0^0, 0, J'' + 1) \leftarrow (0, 0^0, 0, J'')$. We discuss the effect of $\langle \mu_b \rangle$ below.

As seen above, our theoretical treatment predicts that CO_2 has a non-vanishing value of $\langle \mu_b \rangle$ but $\langle \mu_a \rangle = 0$ by symmetry. Consequently, CO_2 has no rotational spectrum with transitions $(0, 0^0, 0, J'' + 1) \leftarrow (0, 0^0, 0, J'')$.² The non-zero value of $\langle \mu_b \rangle$ does not give rise to such a spectrum since it causes transitions with $|\Delta \ell_2| = 1$. We conclude that our theoretical treatment predicts no rotational spectrum for CO_2 in any vibrational state defined by $(v_1, (v_2^{\text{linear}})^{\ell_2}, v_3)$. This is in perfect agreement with conventional spectroscopic wisdom and refutes some of the most vehement protests from Ref. [10].

The authors of Ref. [10] react strongly to our statement that $\langle \mu_b \rangle \neq 0$ for CO_2 and so we will clarify the role played by $\langle \mu_b \rangle$ in the rotation-vibration spectrum of A–B–A molecules such as CO_2 . In Fig. 2 we compare the allowed transitions involving the lowest states with $J = 0$ and 1 for an A–B–A molecule, labelled by linear-molecule and bent-molecule quantum numbers, respectively. As pointed out in Footnote 2 above, the two ^{16}O nuclei in $^{16}\text{O}^{12}\text{C}^{16}\text{O}$ are zero-spin bosons and this molecule will have missing levels as described in Section 8.4 of Ref. [12]. In each vibrational state $(v_1, (v_2^{\text{linear}})^{\ell_2}, v_3)$ only rotation-vibration states of A_1 and A_2 symmetry in the molecular symmetry group $\mathbf{C}_{2v}(\text{M})$ (Table A-5 of Ref. [12]) will exist in Nature and so every second value of J will be missing. Thus, Fig. 2 does not strictly apply to $^{16}\text{O}^{12}\text{C}^{16}\text{O}$, but we can think of the figure as showing the states of $^{17}\text{O}^{12}\text{C}^{17}\text{O}$ for which all J values exist.

The energy levels given in the “BENT-MOLECULE NOTATION” part of Fig. 2 are labelled by the irreducible representations [12] A_1 , A_2 , B_1 , and B_2 (Table A-5 of Ref. [12]) of the molecular symmetry group $\mathbf{C}_{2v}(\text{M})$. When the bent molecule is viewed as a rigid asymmetric top with rotational constants A , B , C , the energies of the three $J = 1$ states are $B + C$, $A + C$ and $A + B$ as indicated. For a linear molecule, it is customary to denote the same group as $\mathbf{D}_{\infty h}(\text{M})$ (Table A-18 of Ref. [12]) and its irreducible representations are denoted $(+s) = A_1$, $(+a) = B_2$, $(-a) = B_1$, and $(-s) = A_2$. In the “LINEAR-MOLECULE NOTATION” part of Fig. 2 the states are labelled accordingly. In linear-molecule theory there is only one rotational constant B and the three $J = 1$ states have the energies $2B$ and $\nu_2 + 2B \pm q$, where ν_2 is the vibrational fundamental energy of the bending mode and q is

² More precisely stated, the rotational spectrum of CO_2 will be extremely weak, gaining intensity from intensity-stealing effects (see Section 14.1.14 of Ref. [12]), and probably not observable. Also, in $^{16}\text{O}^{12}\text{C}^{16}\text{O}$ the two ^{16}O nuclei are zero-spin bosons and the molecule will have missing levels as described in Section 8.4 of Ref. [12].

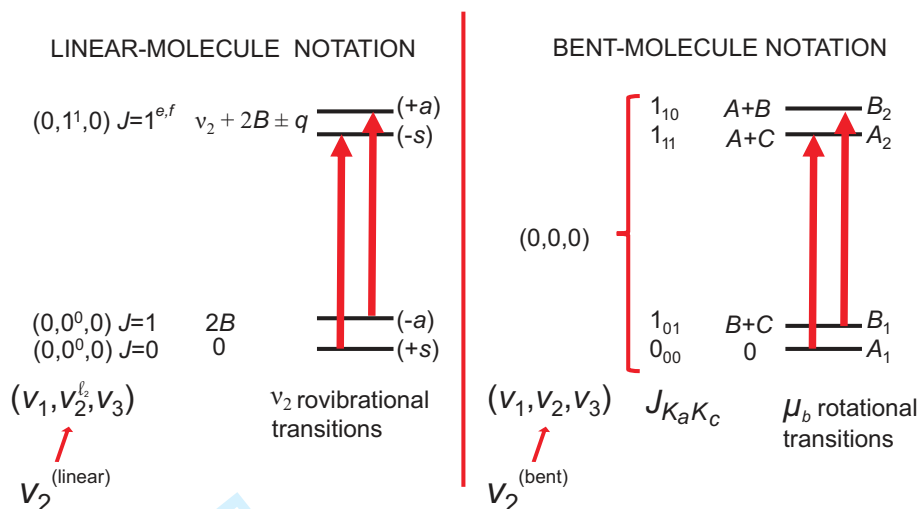


FIG. 2. The transitions involving the lowest states with $J = 0$ and 1 for a triatomic molecule of type A–B–A, labelled in the linear- and bent-molecule schemes, respectively. The A nuclei are *not* zero-spin bosons and so no levels are missing. [12] The correlation between the linear- and bent-molecule labelling schemes is given by Eqs. (1) and (2). The selection rules, in bent-molecule notation, are $|J' - J''| \leq 1$, $J' + J'' \geq 1$, $A_1 \leftrightarrow A_2$, and $B_1 \leftrightarrow B_2$ [12].

the ℓ -doubling constant. The figure clearly suggests that the transition pattern for a linear molecule is identical to that of a bent molecule. The significant difference lies in the sizes of the energy spacings involved. The states of H₂O (whose equilibrium structure is well bent) are labelled in the bent-molecule scheme; the rotational constants are $A \approx 27.9$, $B \approx 14.5$, and $C \approx 9.3$ cm⁻¹. Therefore, the wavenumbers of the two transitions marked in Fig. 2 are $A - C \approx 18.6$ cm⁻¹ and $A + C \approx 37.2$ cm⁻¹; these transitions lie in the microwave region and are logically assigned to the rotational spectrum of H₂O. CO₂ is linear at equilibrium and its states are labelled in the linear-molecule scheme. Since the ν_2 term value is around 667 cm⁻¹, the CO₂ transitions have wavenumbers in the infrared region and are logically assigned to the ν_2 fundamental rotation-vibration band. We have stated above that linear and bent triatomic molecules are not qualitatively different, but they are quantitatively different as we have just demonstrated, using H₂O and CO₂ as examples.

We see that for a well-bent molecule, the non-zero $\langle \mu_b \rangle$ -value gives rise to purely rotational transitions, whereas for a linear molecule, it provides intensity for transitions in the ν_2 fundamental band. Again, this is in perfect agreement with conventional spectroscopic wisdom and contradicts the criticisms of Ref. [10].

III. CONCLUSION

In the present work, I have continued the discussion of the correlation between linear and bent triatomic molecules, started in Section 17.5.2 of Ref. [12], by discussing not only the correlation of the energy levels, but also that of the rotation-vibration transitions. It is shown once again that, contrary to conventional spectroscopic belief, linear and bent triatomic molecules are not qualitatively different. They are, however, quantitatively different since, for example, the b -type transitions with $|\Delta K_a| = 1$ found in the microwave or millimeterwave region for a bent triatomic molecule like H_2O , are moved to the infrared region for a linear triatomic molecule like CO_2 , where they are said to have $|\Delta \ell_2| = 1$ [see Eq. (1)]. Thus, also CO_2 has a non-vanishing averaged b -axis component $|\langle \mu_b \rangle| > 0$ in the vibrational ground state.

We reiterate that the non-zero $|\langle \mu_b \rangle|$ value comes about because

- the b axis is always in the instantaneous molecular plane and so it follows the rotation of the molecule about the a axis, and
- the b axis always points ‘into’ the bond angle of an A–B–C molecule, $0 \leq \angle(\text{A–B–C}) \leq \pi$.

I contend that the question of a triatomic molecule being linear or bent is related entirely to the value of the coordinate $\bar{\rho} = \pi - \angle(\text{A–B–C})$. The instantaneous orientation of the molecule in space, described by the angle χ , is irrelevant in this context. Consequently, an experiment aimed at answering the question as to whether the molecule is linear or bent must measure $\bar{\rho}$ (with a protractor, one could imagine, obtaining a value $0 \leq \bar{\rho} \leq \pi$) and disregard χ . The CEI experiments mentioned above [7, 8] are designed with this in mind.

The authors of Ref. [10] apparently prefer to define the instantaneous molecular geometry in terms of the two Cartesian-type coordinates $(q_a, q_b) \approx \bar{\rho}(\cos \chi, \sin \chi)$ mentioned above. They implicitly argue that if one designs an experiment to measure instantaneous values of (q_a, q_b) , one will obtain average values $(\langle q_a \rangle, \langle q_b \rangle) = (0, 0)$ and seem to infer that therefore, $\langle \bar{\rho} \rangle = 0$. This is fallacious. We discuss in Ref. [9] that the bending–(a -type rotation) wavefunction of triatomic molecules can be written as

$$\psi_{v_2^{(\text{bent})}, \ell_2}(\bar{\rho}, \chi) = \Phi_{v_2^{(\text{bent})}, \ell_2}(\bar{\rho}) \exp(i \ell_2 \chi); \quad (3)$$

this wavefunction is consistent with the volume element $d\bar{\rho} d\chi$ (see also Refs. [3, 15, 16]).

Thus

$$|\psi_{v_2^{(\text{bent})}, \ell_2}(\bar{\rho}, \chi)|^2 = |\Phi_{v_2^{(\text{bent})}, \ell_2}(\bar{\rho})|^2. \quad (4)$$

That is, all values of χ are equally probable, in agreement with the fact that (q_a, q_b) -space is isotropic. Consequently

$$\langle q_a \rangle = \frac{1}{2\pi} \langle \bar{\rho} \rangle \int_0^{2\pi} \cos \chi d\chi = 0 \quad (5)$$

and

$$\langle q_b \rangle = \frac{1}{2\pi} \langle \bar{\rho} \rangle \int_0^{2\pi} \sin \chi d\chi = 0 \quad (6)$$

where

$$\langle \bar{\rho} \rangle = \int_0^\infty \bar{\rho} |\Phi_{v_2^{(\text{bent})}, \ell_2}(\bar{\rho})|^2 d\bar{\rho}. \quad (7)$$

One sees from Eqs. (5) and (6) that $(\langle q_a \rangle, \langle q_b \rangle) = (0, 0)$ does not automatically imply $\langle \bar{\rho} \rangle = 0$. Eqs. (5) and (6) only allow the conclusion that as we already know, there is no preferred direction in (q_a, q_b) -space. With $(\langle q_a \rangle, \langle q_b \rangle) \neq (0, 0)$, we could identify a preferred direction. Thus, from the result $(\langle q_a \rangle, \langle q_b \rangle) = (0, 0)$ we cannot derive the average structure of the molecule. In order to do this, we must determine the probability distribution of (q_a, q_b) and then calculate the average of $\bar{\rho}$ taking into account that the probability of finding this coordinate in the interval $[\bar{\rho}, \bar{\rho} + d\bar{\rho}]$ is equal to the probability of finding the instantaneous value of (q_a, q_b) between two concentric circles with radii $\bar{\rho}$ and $\bar{\rho} + d\bar{\rho}$, respectively, centered at the origin of the (q_a, q_b) plane. In this manner, we compute average values $\langle \bar{\rho} \rangle > 0$ which coincide with our values, calculated in terms of $(\bar{\rho}, \chi)$ -dependent wavefunctions. Consequently, also the theoretical description preferred by the authors of Ref. [10] leads to bent average structures of linear triatomic molecules.

It is instructive to compare the relationship between the coordinates (q_a, q_b) on one hand and $(\bar{\rho}, \chi)$ on the other hand for a linear molecule with the coordinates customarily used to describe the hydrogen atom. It is clearly legitimate to treat the H atom using for the electron the coordinates (x, y, z) in a Cartesian axis system with the proton at $(0, 0, 0)$, but in the traditional theoretical treatment one normally transforms to the spherical coordinates (r, θ, ϕ) , where

$$(x, y, z) = r (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta). \quad (8)$$

The wavefunction of the ground state for the hydrogen atom is, in the customary ψ_{nlm} notation for $(n, \ell, m) = (1, 0, 0)$, $\psi_{100}(r, \theta, \phi) = R_{10}(r) Y_{00}(\theta, \phi) = R_{10}(r)/\sqrt{4\pi}$ since $Y_{00}(\theta, \phi) = 1/\sqrt{4\pi}$. For an actual hydrogen atom (where the nucleus is a proton with $Z = 1$), we have $R_{10}(r) = (2/a_0^{3/2}) \exp(-r/a_0)$ with the Bohr radius $a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$ where m_e is the electron mass and the other symbols have their usual meanings. The wavefunction $\psi_{100}(r, \theta, \phi)$ is normalized with the volume element $dV = r^2 dr \sin\theta d\theta d\phi$. In consequence, we obtain the averages

$$\langle x \rangle = \frac{1}{4\pi} \langle r \rangle \int_0^\pi \sin^2\theta d\theta \int_0^{2\pi} \cos\phi d\phi = 0, \quad (9)$$

$$\langle y \rangle = \frac{1}{4\pi} \langle r \rangle \int_0^\pi \sin^2\theta d\theta \int_0^{2\pi} \sin\phi d\phi = 0, \quad (10)$$

$$\langle z \rangle = \frac{1}{4\pi} \langle r \rangle \int_0^\pi \cos\theta \sin\theta d\theta \int_0^{2\pi} d\phi = 0, \quad (11)$$

where

$$\langle r \rangle = \int_0^\infty dr r^3 |R_{10}(r)|^2. \quad (12)$$

The ground state wavefunction for the H atom, the 1s orbital $\psi_{100}(r, \theta, \phi)$, acquires its maximum value at $r = x = y = z = 0$ and all three averages $\langle x \rangle = \langle y \rangle = \langle z \rangle = 0$ because in the 1s state, the electron positions (x, y, z) and $(-x, -y, -z)$ are equally probable. In practice, vanishing integrals over ϕ cause $\langle x \rangle = \langle y \rangle = 0$ in Eqs. (9) and (10), respectively, and a vanishing integral over θ causes $\langle z \rangle = 0$ in Eq. (11).

Do the results in Eqs. (9)–(11) imply that it is meaningful to think of the H atom having the electron placed right on top of the proton? No, they do not! It is well known from introductory physics or physical chemistry that in the 1s state, the most probable proton-electron distance (i.e., the value of r at which the radial distribution function $r^2 |R_{10}(r)|^2$ attains its maximum value) is the Bohr radius a_0 , and that the average proton-electron distance, $\langle r \rangle = 3a_0/2$. These values are calculated by considering that the probability of finding the proton-electron distance between r and $r + dr$ equals to probability of finding the electron in the volume between two spheres in xyz -space, each centered at $x = y = z = 0$ and with radii of r and $r + dr$, respectively. We remark that also for the H atom, the result $\langle x \rangle = \langle y \rangle = \langle z \rangle = 0$ is the only one consistent with the isotropy of xyz -space, and it does not imply $\langle r \rangle = 0$. This observation is exactly analogous to the conclusion made above for the linear molecule: The fact that $(\langle q_a \rangle, \langle q_b \rangle) = (0, 0)$ does *not* imply $\langle \bar{\rho} \rangle = 0$.

Obviously a useful mental image of the hydrogen atom in the 1s state is one of a proton and an electron at a distance of $3a_0/2$, this being the average distance, and the line connecting the two particles defining a direction in space which, however, is irrelevant for the *structure* of the atom which only depends on r . Similarly, in a useful mental image of the triatomic molecule A–B–C, the molecule has a bent average structure defined by the values $\langle \bar{\rho} \rangle > 0$, $\langle r_{AB} \rangle$, and $\langle r_{BC} \rangle$. The angle χ defines a direction in space which, however, is irrelevant for the structure of the molecule so that we can simply ignore it in this context.

The present work refutes the sweeping statements made about our previous work [1–5] by the authors of Ref. [10]. The concluding sentence of Ref. [10] is “Never attempt to observe the b -component of the permanent dipole of CO_2 .” The irony is that the b -axis dipole moment component of CO_2 has, in fact, already been observed. Johns and Vander Auwera [17] measured absolute intensities of the transitions in the ν_2 band, obtaining a transition moment square for this band of $|M_{\perp}^{(\text{tr})}|^2 = 0.032938(48) \text{ D}^2$. Eq. (20) of Ref. [9] yields $\langle \mu_b \rangle = 0.1818(1) \text{ D}$, in satisfactory agreement (deviation around 10%, which is not unreasonable for intensity measurements) with the theoretical value of 0.1634 D from Ref. [9]. For the linear molecule HCN, the intensities of rotation-vibration transitions in the ν_2 band have been measured several times and $\langle \mu_b \rangle$ -values of 0.1798(17) [18], 0.1781(1) [19], and 0.169(1) D [20] have been determined. Very recently, Hirano *et al.* [21] have computed a theoretical value of 0.17607 D, differing between 1.1 and 4.0% from the experimental values.

In typical rotational-spectroscopy parlance one says that if, for a given molecule, the b -component of the dipole moment vanishes at the equilibrium geometry, the molecule has no b -type spectrum rotational spectrum. The authors of Ref. [10] obviously, in their concluding sentences, erroneously take this to mean that, since CO_2 has no *rotational* b -type spectrum (which is correct), it has no b -component of the permanent dipole moment. CO_2 *has* a b -type spectrum but, as we have discussed above, in linear-molecule terminology we normally do not call this a rotational spectrum; the most prominent b -type transitions belong to the linear-molecule ν_2 band and are in the infrared region.

I hope that with the present work, I have managed to convince the authors of Ref. [10] that the average structure of a linear triatomic molecule is indeed bent, and that CO_2 and HCN have $\langle \mu_b \rangle \neq 0$ and, therefore, b -type infrared transitions in their respective ν_2 bands. Also, I hope to have made it clear that, as argued in 1998 in Section 17.5.2 of Ref. [12], linear and bent chain molecules are not qualitatively different. One can understand the

linear-molecule energy-level pattern, and the associated spectrum, as a limiting case of the bent-molecule energy-level pattern and spectrum.

The Inuit people of northern Canada and Greenland always end their tales in the same manner. I would like to quote their wording here, hoping that the authors of Ref. [10] share the sentiment:

“We have now come to the end of our story, and so we will now stop.”

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