ENERGY LEVELS OF TRIATOMIC MOLECULES OF THE SLIGHTLY ASYMMETRIC-TOP TYPE IN DEGENERATE ELECTRONIC STATES \((^2\Pi)\) AND THE GEOMETRICAL CONFIGURATION OF THE MOLECULE \(\mathrm{CO}_2^+\)

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ENERGY LEVELS OF TRIATOMIC MOLECULES OF THE SLIGHTLY ASYMMETRIC-TOP TYPE IN DEGENERATE ELECTRONIC STATES ($^2\Pi$) AND THE GEOMETRICAL CONFIGURATION OF THE MOLECULE CO_2^+

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A linear triatomic molecule in a $^2\Pi$ electronic state behaves in a way entirely analogous to diatomic molecules, provided that no vibrations other than totally symmetric ones are excited in it. As Renner showed ([1]), excitation of a bending vibration in linear molecules leads to the appearance of a vibrational angular momentum l, directed parallel to the molecular axis and interacting with the electronic orbital angular momentum L. As a result of this interaction, the electron-vibrational level is split into two substates with $K = \Lambda + l$ and $K = \Lambda - l$. A detailed treatment of such splitting (the "Renner effect") for a linear triatomic molecule in a $^2\Pi$ electronic state was carried out in ([2]).

It is also known that a slightly bent molecule has two almost equal principal moments of inertia ($I_B \approx I_C$), while the third moment I_A is considerably smaller than these. The rotational levels of such a slightly asymmetric top, neglecting the correction for centrifugal distortion, can be represented by the expression ([3])

$$F(J,K) = \frac{1}{2}(B+C)J(J+1) + \left[A - \frac{1}{2}(B+C)\right]K^2 =$$

$$= \widetilde{B}J(J+1) + (A-\widetilde{B})K^2, \qquad (1)$$

i.e., by the formula for a symmetric top with a certain effective value of the rotational constant $\widetilde{B} = \frac{1}{2}(B+C)$.

In ([4]) it was shown that, in outward appearance, a transition between two linear electronic states is very similar to a transition in which the molecule is linear in one state and slightly bent in the other. However, in the bent state the molecule is in fact an asymmetric top, and therefore a doubling of the rotational levels

(of K-type) should be observed, similar to the Λ-doubling in linear molecules, but considerably larger in absolute magnitude, since it is caused by the motion of heavy nuclei.

It can be shown that a linear–linear transition must differ from a linear–bent transition not only by the presence of asymmetric doubling (of K-type). Indeed, if in a linear molecule the vibrational angular momentum l appears only upon excitation of a bending vibration, then in a slightly bent molecule, during its rotation, there exists a nuclear orbital angular momentum G, whose projection onto the molecular axis l may be nonzero even when bending vibrations are not excited.

The subsequent reasoning is entirely analogous to the treatment carried out in ([1],[2]). In a bent molecule in a Π-electronic state, the moment G can interact with the electronic moment L. Different mutual orientations of the projections of these vectors on the molecular axis (l and Λ)

must also in this case lead to a splitting of the electronic level into substates with different values of $K = (\Lambda + l)$. Thus, for a slightly bent molecule one should observe a phenomenon analogous to the Renner effect in linear molecules. This time, however, the splitting is not associated with the excitation of deformation vibrations.

Let us now consider in more detail the doubling of rotational levels caused by the asymmetry of the molecule. As Wang showed [(5)], such doubling, both in absolute magnitude and in the form of its dependence on J, is determined by the magnitude of the projection on the axis of the angular momentum due to the motion of the nuclei, i.e., by the value of l. For $l = 1$ or 2, Wang' s formula has the form

$$\Delta\nu = \frac{1}{8^{l-1}} \left[\frac{C-B}{2A-C-B}\right]^{l} \left[A - \frac{1}{2}(B+C)\right] \frac{(J+l)!}{(J-l)!}. \qquad (2)$$

We note that the Λ-doubling depends on J and Λ in an analogous way (see, for example, [(6)]). Of course, in this case, instead of l one uses the quantum number $\Omega = |\Lambda + \Sigma|$, where Σ is the projection on the axis of the electronic spin angular momentum.

We give the dependence on J for asymmetric doubling (l) and Λ-doubling (Ω).

l, Ω	$\frac{1}{2}$	1	$\frac{3}{2}$	2
$f(J)$	$J + \frac{1}{2} \approx J$	$J(J+1) \approx J^2$	$(J^2 - \frac{1}{4})(J + \frac{3}{2}) \approx J^3$	$J(J^2-1)(J+2) \approx J^4$.

Since l can be only an integer, while Ω can be either an integer or a half-integer, in some cases one can distinguish one type of doubling from the other not only by its absolute magnitude but also by the form of its dependence on J. For

example, for $^2\Pi$-states $\Omega = 1/2$ and $3/2$, while $l = 0, 1, ...$ If the molecule differs only slightly from a linear one, then the coefficient before $(J+l)!/(J-l)!$ in (2) may be very small, and the observed asymmetric doubling can easily be taken for Λ-doubling. However, for $^2\Pi$-states the Λ-doubling is proportional to J or J^3, whereas the asymmetric doubling is proportional to J^2 or J^4.

It is known that in $^2\Pi_{3/2}$-states the Λ-doubling is very small in absolute magnitude and is often practically not observed even for rather large J. Therefore, the observation of a doubling proportional to J^2 is a quite definite indication that we are dealing with asymmetric doubling and that, consequently, the molecule is bent in one of the states.

In the $^2\Pi_{1/2}$-states of linear molecules the Λ-doubling is proportional to $J+1/2$ and is very large even at small J. In the case of a slightly bent molecule, apparently, the superposition of two types of doubling is possible, and the dependence on J will no longer be linear.

In the works [7], the rotational structure of a very large number of bands of the system $A^2\Pi_u - X^2\Pi_g$ of the molecule CO_2^+ was measured. The author carried out a vibrational and rotational analysis on the assumption that the molecule is linear in both states. However, in a number of bands an anomalous doubling of the rotational levels was found, and the vibrational level $\nu_1 = 1$ in the $X^2\Pi_{3/2}$-state was split into two sublevels.

Mrozowski [7] provisionally explains all anomalies in the spectrum of CO_2^+ by perturbations. However, apparently, it will be more correct to explain them on the basis of the considerations given above.

In work [7b] it was found that the level $1^200\,(X^2\Pi_{3/2})$ has, anomalously for a linear molecule, a doubling of the rotational levels proportional approximately to J^2, and the exponent also increases somewhat with increasing J. The dependence of the doubling on J^2 allows us to conclude that the projection of the angular momentum responsible for the doubling is equal to unity. Obviously, this can only be the number l, since in $^2\Pi$-states Ω is half-integer, and we are dealing with a molecule slightly bent in the ground state.

As follows from (2), the asymmetric splitting for $l = 1$ is equal to

$$\Delta\nu = \frac{1}{2}(B - C)J(J + 1). \tag{3}$$

Substituting this expression into (1) and taking into account that in the CO_2^+ molecule there are no asymmetric components of the rotational levels (because the nuclear spin of the oxygen atoms is zero), we obtain, for even (or odd) values of J,

$$F(J, 1) = \left[A - \frac{1}{2}(B + C)\right] + \widetilde{B}_1 J(J + 1),$$

Fig. 1. Dependence of $\Delta_2 F(J)/(J+1/2)$ on $(J+1/2)^2$ for the 1^a00 level $\left(X^2\Pi_{3/2}\right)$ of the CO_2^+ molecule according to data from ([76]).

Figure 1: Fig. 1. Dependence of $\Delta_2 F(J)/(J+1/2)$ on $(J+1/2)^2$ for the 1^a00 level $\left(X^2\Pi_{3/2}\right)$ of the CO_2^+ molecule according to data from ([76]).

and for odd (or even) values,

$$F(J,1) = \left[A - \frac{1}{2}(B+C)\right] + \widetilde{B}_2 J(J+1),$$

where $\widetilde{B}_1 = \frac{1}{4}(3B+C)$, and $\widetilde{B}_2 = \frac{1}{4}(B+3C)$.

Taking into account the correction for centrifugal perturbation, we write the combination differences in the form

$$\Delta_2 F(J) = 4\widetilde{B}(J+1/2) - 8D(J+1/2)^3. \tag{4}$$

It is obvious that if one represents graphically the dependence of $\Delta_2 F(J)/(J+1/2)$ on $(J+1/2)^2$, one obtains a straight line intersecting the ordinate axis at the point $4\widetilde{B}$ and with slope tangent equal to $-8D$ ([8]). Figure 1 shows a plot constructed from the averaged values of $\Delta_2 F(J)$ from Ref. ([76]). Points a correspond to even values of $J+1/2$, points b to odd ones. It is seen from the plot that the points for even $J+1/2$ lie lower than those for odd ones. (Points for small values of J are not taken into account, since apparently they have low accuracy.) Linear extrapolation through points with mean values of J gives the values $\widetilde{B}_1 = 1.5022$ cm^{-1} and $\widetilde{B}_2 = 1.5006$ cm^{-1}. The scale of the plot permits these quantities to be determined with an accuracy of ± 0.0004 cm^{-1}. Therefore the rotational constants are: $B = 0.3757 \pm 0.0002$ cm^{-1} and $C = 0.3749 \pm 0.0002$ cm^{-1}.

Fig. 1. Dependence of $\Delta_2 F(J)/(J+1/2)$ on $(J+1/2)^2$ for the 1^a00 level $\left(X^2\Pi_{3/2}\right)$ of the CO_2^+ molecule according to data from ([76]).

For a symmetric triatomic molecule XY_2 the relation holds

$$\operatorname{ctg}^2 \frac{\alpha}{2} = \frac{2m_Y + m_X}{m_X}\left(\frac{B}{C} - 1\right),$$

where α is the angle YXY, m_X is the mass of atom X, and m_Y is the mass of atom Y. The OCO angle in the CO_2^+ molecule, calculated from this expression, is $168 \pm 3^\circ$ (the maximum error is given for the accuracy estimate indicated above in the determination of the quantities $\widetilde{B}_1$ and $\widetilde{B}_2$). This angle corresponds to a distance $r(CO) = 1.1830 \pm 0.0004$ Å.

Special attention should be paid to the negative value of the constant D in (4) (in the plot the straight line rises with increasing J). This clearly indicates that the effective moment of inertia decreases as the rotation accelerates. One may try to explain the anomalies in the spectrum of CO_2^+ by some kind of perturbations, but, apparently, this fact remains incomprehensible if one starts from the assumption that the molecule is linear. On the other hand, an explanation is easy to find if the CO_2^+ molecule is considered bent. Indeed, upon rotation of an angular molecule about the A axis

centrifugal forces decrease the angle O–C–O, while the moment of inertia I_A increases. At the same time the distances of the oxygen atoms from the B and C axes decrease and, consequently, the values of I_B and I_C decrease, which is manifested in the negative value of D.

The angular model of CO_2^+ also makes it possible to explain the fact that the splitting of the rotational levels increases somewhat faster than J^2. Since, in rotation about the A axis, the angle decreases under the action of centrifugal forces, $B - C$ increases with increasing J (the asymmetry of the molecule increases). Therefore in expression (3) the coefficient before $J(J+1)$ is no longer a constant quantity, but also depends on J. This is easy to understand, since in expressions (2) and (3) centrifugal perturbations are not taken into account in any way, and they are applicable only to a rigid rotator.

Mrozowski, in work ([7]), also observed an anomalous Λ-doubling of the vibrational level with $v_1 = 2\left(X^2\Pi_{1/2}\right)$. The author suggested that the observed doubling should be regarded as the result of the superposition of doublings of two types: a type linearly dependent on J, and a type approximately proportional to $J^{2.5}$. Apparently, for this level too $l = 1$, and the observed doubling is in reality the result of the superposition of Λ-doubling and asymmetric doubling.

Apparently one cannot agree with the conclusion of the author of the cited papers that the level $v_1 = 4\left(A^2\Pi_{3/2}\right)$ is split into two sublevels. As is seen from Delandre's table in work ([7]), the values $\Delta G'_{v+1/2}$ decrease only slightly and quite monotonically in passing from $v = 0$ to $v = 3$. Therefore the band 33022 cm^{-1} ($4^b, 0$ in Mrozowski) should, in all probability, be regarded as the 400–000 band, while the bands 32964 cm^{-1} ($4^a, 0$) and 31722.9 cm^{-1} ($4^a, 1^a$) are associated with the transitions 320–000 and 320–$(100)^1$, respectively. Confirmation of such an assignment may be seen in the fact that in this case the frequency ν'_2 proves to be equal to 531 cm^{-1} (from other bands Mrozowski estimates $\nu'_2 < 560$ cm^{-1}).

Thus, in the excited electronic state $A^2\Pi$ there are apparently no anomalies similar to those considered above (at least in the $A^2\Pi_{3/2}$ substate). Therefore there is no basis for regarding this state as nonlinear.

In the cited works on CO_2^+, no other vibrational levels were found in which the doubling of rotational levels would be proportional to J^2. This is probably connected with the large value of the angle O–C–O. Since in linear molecules levels with $l = 1$ are absent (for $v_2 = 0$) and, on the other hand, the principle of

continuity of the change of properties in passing from angular to linear molecules must evidently be observed, one may suppose that the larger the angle at the central atom, the less likely it is that levels with $l \neq 0$ are excited.

Thus, the consideration presented makes it possible to explain a number of anomalies in the spectrum of the CO_2^+ molecule. At the same time it apparently is not in contradiction with the main results of Mrozowski' s vibrational analysis. As for the rotational constants, the effective values $\widetilde{B} = \frac{1}{2}(B+C)$ were evidently determined.

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Note: Figure translations are in progress. See original paper for figures.