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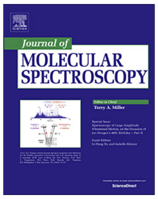

Assignment of the photoelectron spectrum of the nitrate anion NO_3^- and vibronic interactions in the nitrate free radical

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ABSTRACT

The unpaired electron orbital of NO_3 is of a'_2 symmetry in the ground electronic state, and thus its motion about the symmetry axis of the molecule is free rotation. When a degenerate vibration is excited, however, the free azimuthal rotation of the unpaired electron is perturbed much by nuclear motions of the degenerate mode, as evidenced by high-resolution spectroscopic studies. Thus the ν_4 fundamental state, for example, bears some characters of the $\tilde{B}$ excited electronic state through the Herzberg-Teller (H-T) interaction, and Neumark et al. explained anomalous ν_4 progression in the photoelectron spectra of the NO_3^- anion by the H-T mechanism. However, the interaction parameter Neumark required was too large to reproduce the ν_4 molecular parameters in the ground electronic state precisely determined by high-resolution IR spectroscopy. This discrepancy was resolved by the fact that the upper ν_4 overtone/-combination states of Neumark's photoelectron transitions were primarily of vibrational in nature. The present study thus showed that NO_3 bears both vibrational and H-T induced electronic characters in excited states of degenerate modes in the ground electronic state.

1. Introduction

Molecular spectroscopic studies on the nitrate free radical started early in 1980′s using laser-induced-fluorescence/dispersed fluorescence (LIF/DF) [1,2] and high-resolution infrared spectroscopy [3–5] and established the molecular geometry of the NO_3 molecule in the ground vibronic state to be of D_{3h} symmetry with four normal mode frequencies: ν_1 $(a'_1) = 1060$, ν_2 $(a''_2) = 762.327$, ν_3 $(e') = 1492.393\ 57$, and ν_4 $(e') = 365.483\ 92\ \mathrm{cm}^{-1}$ (the symmetry of the vibrational state does not include that of the ground electronic state A'_2, i.e. it represents only that of the vibration). This vibrational assignment for the NO_3 neutral is hereafter referred to as Assignment I.

A little later Neumark and his collaborators (abbreviated as WABN) [6] reported an important result on the NO_3 molecular system obtained by using a different method, namely they observed the photoelectron spectrum of the NO_3^- anion. A most remarkable feature of this study was that the photoelectron spectrum exhibited an anomalous progression in ν_4 in addition to the normal one in ν_1, as reproduced in Table 1. The peak at 363 cm^{-1} next to the main one was ascribed to the first excited state of the ν_4 mode, which was regarded as a most conclusive evidence for the $\Delta\nu_4 = 1$ transition. Neumark explained this anomaly by the vibronic interaction between the $\tilde{X}^2A'_2$ ground and $\tilde{B}^2E'$ excited electronic states of NO_3 through the ν_4 mode, i.e. the Herzberg-Teller (hereafter abbreviated as H-T) interaction. He required the H-T parameter larger than 2339 cm^{-1}, but thought the interaction was weak enough that the NO_3 $\tilde{X}^2A'_2$ ground state still had D_{3h} symmetry. Mayer et al. [7] then performed molecular electronic energy calculations to support Neumark's vibronic interaction mechanism. They found that the potential energy surface (PES) they derived had a small hump 0.006 eV (48 cm^{-1}) high at the D_{3h} center. More recently Stanton [8,9] calculated from the PES of Mayer et al. the normal mode frequencies and some vibrational anharmonicity constants. A most striking result of Stanton was the ν_3 frequency to be about 1000 cm^{-1}, nearly 500 cm^{-1} lower than the value of Assignment I. Jacox and her collaborators [10,11] observed and analyzed infrared spectra of NO_3 trapped in low-temperature rare-gas matrices, in particular those of nitrogen and oxygen isotopes substituted NO_3, and concluded the Stanton low ν_3 frequency to be correct and proposed the 1492 cm^{-1} band to be reassigned to $\nu_3 + \nu_4$. This vibrational assignment will be called Assignment II. Some of vibrational anharmonicity constants Stanton [9] calculated from the PES of Mayer et al. [7] were, however, too large in magnitude to reproduce the changes of the B and C rotational constants upon ν_4 mode excitation and also the ℓ-type doubling constant $\boldsymbol{q_4}$ in the ν_4 state, precisely determined by high-resolution infrared

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Table 1
The 266 nm photoelectron spectrum of the NO_3^- anion, observed by Weaver et al. [6].

Observed peak position (in cm^{-1})	Intensity[a]	Assignment[b]	
		NO_3 (v_1', v_4') ← NO_3^- (v_1'', v_4'')	
		WABN [6]	YR [13]
−661	0.017		
−339	0.063	(0, 1) ← (0, 1)	(0, 1) ← (0, 1)
0	0.416	(0, 0) ← (0. 0)	(0, 0) ← (0. 0)
363	**0.171**	**(0, 1) ← (0, 0)**	**(0, 3) ← (0, 1)**
758	0.096	(0, 2) ← (0, 0)	(0, 2) ← (0, 0)
1057	0.336	(1, 0) ← (0, 0)	(1, 0) ← (0, 0)
1420	**0.096**	**(1, 1) ← (0, 0)**	**(0, 4) ← (0, 0)**
1831	0.060	(1, 2) ← (0, 0)	(1, 2) ← (0, 0)
1936	0.080		
2162	0.122	(2, 0) ← (0, 0)	(2, 0) ← (0, 0) (0, 6) ← (0, 0)
2387	0.037		
2557	0.068		

[a] Read out by E. Hirota from Fig. 2 of Ref. [6] and given in an arbitrary scale.
[b] Only strong components are listed.

spectroscopy, as pointed out by Hirota [12]. These findings clearly indicated that the H-T interaction parameters of [6,7] were too large.

In 2016 Yamada and Ross [13] reported that the photoelectron spectra of WABN could be explained by "allowed", i.e. Δv_4 = even transitions only, as shown in Table 1. The most critical point to be examined carefully in the YR assignment was interpretation of the peak at 363 cm^{-1}; YR ascribed this rather distinct and eminent peak to the hot band: (0, 3) ← (0, 1), but it might not be strong enough to match the observed intensity. The YR assignment also differed from the WABN one in the peak at 1420 cm^{-1}; the upper state of this line was assigned to ($v_1 = 1$, $v_4 = 1$) in WABN to be compared with ($v_1 = 0$, $v_4 = 4$) in YR (note that the v_1 frequency is nearly three times larger than that of v_4). The rest of the two assignments was more or less the same. We may thus say that the assignment of YR [13] is as plausible as that of WABN [6]; the standard deviation of the fits was 24.6 and 25.4 cm^{-1}, respectively. It should be noted that many of the upper states of the photoelectron spectra were overtones or combination states involving the v_4 mode, and WABN appealed to the H-T mechanism, which transferred the $\tilde{B}$ state character to the v_4 vibrational manifold in the ground electronic state, whereas YR relied on allowed transitions to v_4 overtone/combination states. The photoelectron spectra reported in [6] were unfortunately neither detailed nor precise enough to decide which assignment was more realistic. So we will take into account the two approaches in an appropriate proportion to explain the observed spectra, without deteriorating much the spectral fit. The present study will proceed comparison of the two assignments: WABN and YR further by fully exploiting all the observed data not only of photoelectron but also of LIF/DF and IR, in order to clarify the nature of vibronic interactions in the NO_3 molecule, as described in the following sections.

2. The v_4 fundamental state of neutral NO_3 in the ground electronic state

Hirota [12] noticed that the first-order Coriolis coupling constant ζ and spin-orbit interaction constant a_{eff} are closely correlated with each other in the four vibrational states of e' symmetry: v_4, $v_1 + v_4$, v_3, and $v_1 + v_3$. It should be stressed that these findings hold only for Assignment I. Furthermore, he found that a few molecular parameters like centrifugal distortion constants D_N and D_{NK} and inertial defect observed for the ground vibronic state were well reproduced, if the observed first-order Coriolis coupling constant rather than the force-field calculated ζ value was employed, and that the ζ_3 and ζ_4 observed values satisfied the sum rule: $\zeta_3 + \zeta_4 = 0$ closely, as predicted by the vibration-rotation interaction theory. Table 2 lists the harmonic force field and compares the calculated and observed values of the inertial defect and centrifugal distortion constants. Here the two sets of "calc" were *calculated* from the two force fields, which were set up by combining the four normal mode frequencies with the first-order Coriolis coupling constants: IR observed (0.193) and force-field calculated (0.7). These evidences led Hirota to conclude that, although the unpaired electron occupied an orbital of a_2' symmetry in the ground electronic state, its azimuthal motion about the symmetry axis of the molecule, which was otherwise completely free, was affected considerably by a degenerate vibrational mode when singly excited. Namely the unpaired electron follows the movements of the nuclear framework closely. Hirota thus proposed that the excited state of degenerate vibrations was most reasonably represented by a superposition of two wavefunctions as follows:

$$C_1^{(10)}|\ell=\pm1,\quad \Lambda=0\rangle + C_1^{(01)}|\ell=0,\quad \Lambda=\pm1\rangle. \tag{1}$$

It should be noted that here neither the vibrational angular momentum quantum number ℓ nor the electronic one Λ, but the total $\bar{\Lambda} = \ell + \Lambda$ played the role, and both of the two wavefunctions belong to $\bar{\Lambda} = \pm1$. In fact, as already remarked, the observed first-order Coriolis coupling constant comprised both the vibrational and electronic components, and, when combined with the normal mode frequencies, described the vibrational modes precisely. On the other hand, the effective spin-orbit interaction constants divided by the Coriolis coupling constants led to the spin-orbit interaction constant A_{SO} of about 1 cm^{-1}, much smaller than the value estimated for the constant in the $\tilde{B}$ excited state of 30–50 cm^{-1}. It is because the second term in Eq. (1) contributes much less than the first term does to the v_4 state.

We must be careful of the fact that the second term of Eq. (1) is not exactly identical to the $v_4 = 0$ of the $\tilde{B}$ excited state manifold, because it represents a state of the unpaired electron caused by the nuclear motions of degenerate vibrational mode. However, we may try to employ the H-T mechanism and derive an approximate or trial expression for a_{eff}:

$$a_{eff} = (|h_1|^2/E^2)A_{SO}, \tag{2}$$

as done by Hirota et al. [14], which led to h_1: the H-T parameter of 888 cm^{-1}, where E: the excitation energy of the $\tilde{B}$ state of 15,100 cm^{-1} and A_{SO} of 50 cm^{-1} were employed. This H-T interaction constant is much smaller than the value of WABN: 2339 cm^{-1}, in agreement with the supposition of the preceding section that both the WABN and YR mechanisms contributed to the observed photoelectron spectra. Hirota [14] also showed that the fundamental v_4 frequency was reduced by the H-T interaction by $2|h_1|^2/E$, which was

Table 2
Harmonic force field and comparison of the calculated *vs* observed inertial defect and centrifugal distortion constants.

Harmonic force field for $^{14}NO_3$			
F_{11} (md/Å)	10.449	F_{22} (mdÅ)	0.8450
F_{33} (md/Å)	7.392/7.956[a]	F_{44} (mdÅ)	0.4139/0.3959[a]
F_{34} (md)	0.0/−0.3[a]		
	Calc		obs
ζ_3	0.193[b]	0.7[c]	
Inertial defect (uÅ^2)	0.2221	0.2585	0.2193 (64)
D_N (10^{-5} cm^{-1})	0.1069	0.1421	0.1058 (49)
D_{NK} (10^{-5} cm^{-1})	−0.1965	−0.2667	−0.162 (11)

[a] Two sets are listed.
[b] Observed value.
[c] Value calculated from the harmonic force field with F_{34} = 0.0 md.