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On the Determination of a Heterogeneous vs a Homogeneous Perturbation in the Spectrum of a Diatomic Molecule: The $K^1\Sigma^+$, $v = 0$ state of $^{13}C^{18}O$

K. S. E. EIKEMA, W. HOGERVORST, AND W. UBACHS

Laser Centre, Department of Physics and Astronomy, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

A spectrum of the $K^1\Sigma^+$, $v = 0$ state of $^{13}C^{18}O$, excited by XUV-laser radiation, has been recorded. It turns out to be an exemplary case of a strongly perturbed rotational manifold without direct spectroscopic information on the perturber state. The question of the nature of a perturbation, i.e., whether it is *heterogeneous* or *homogeneous*, is addressed. From a numerical analysis it follows that the perturbation of the $K^1\Sigma^+$, $v = 0$ state is heterogeneous and that the perturber may be tentatively identified as the $E^1\Pi$, $v = 5$ state. Precise values for the molecular constants are determined for both the $K^1\Sigma^+$, $v = 0$ and the perturber state.

1. INTRODUCTION

The rotational structure of highly excited states of diatomic molecules is often found to be perturbed. Experimentally these perturbations may manifest themselves in many ways, e.g., missing lines or sudden changes in the intensity of particular lines, deviations from regular line patterns with nearly equidistant spacings, and line narrowing or broadening effects. In the analysis a perturbed level structure reveals itself as a deviation from a simple polynomial expression for the rotational or vibrational energy progressions. Perturbations in the spectra of diatomic molecules, experimental observations, various parametrization procedures and physical interpretations have been treated in numerous investigations. In the recent book by Lefebvre-Brion and Field (*1*) an overview of this research field is given as well as a thorough theoretical framework.

Phenomenologically a distinction is made between homogeneous and heterogeneous perturbations. In the former case an interaction parameter may be defined that is independent of the rotational quantum number J, while in the latter case it depends on J. Homogeneous perturbations may occur as electrostatic or nonadiabatic interactions between states of the same electronic symmetry, although spin–orbit interaction may cause a homogeneous perturbation between states with different electronic symmetry. Heterogeneous perturbations are generally found between rovibrational manifolds with different electronic symmetry.

A celebrated example of a deperturbation treatment based on homogeneous interactions is that of Stahel *et al.* (*2*), who analyzed the vibronic structure of valence and Rydberg states of molecular nitrogen. $^1\Sigma_u^+$ and $^1\Pi_u$ states were treated separately, including homogeneous perturbations between vibronic states, and large shifts of the vibrational band origins were explained. A typical example of a heterogeneous perturbation is that of l-uncoupling between $^1\Sigma^+$ and $^1\Pi$ Rydberg states. These states are connected to molecular orbital configurations that differ only by a single orbital, namely that of the Rydberg electron. Well known is the l-uncoupling treatment of $c_n\ ^1\Pi_u$ and $c_{n+1}\ ^1\Sigma_u^+$ Rydberg states, again in molecular nitrogen (*3*). The examples mentioned

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constitute cases where the entire rotational manifold of a vibronic state is affected by the perturbation.

In addition, local perturbation effects, where the rotational level structure appears in the form of an anticrossing around a certain J value, may be found. Numerous examples have been reported in the literature (see Lefebvre-Brion and Field (*1*)). Particularly of note is the deperturbation procedure described by Yoshino and Freeman (*4*) for part of the N_2 spectrum involving a multitude of local interactions, homogeneous as well as heterogeneous. These local effects with anticrossing patterns occur only when both mutually interacting states are bound, so that the energies of rotational states are well defined.

Generally, local perturbations are accompanied by the appearance of known perturber states in the spectrum. In such cases the nature of the perturbation, homogeneous or heterogeneous, follows straightforwardly. The question arises whether the electronic symmetry of the perturber manifold may be deduced, even if it is not observed. In the present investigations of highly excited states of carbon monoxide (*5–7*) the intriguing example of the $K(4p\sigma)^1\Sigma^+$, $v = 0$ state of $^{13}C^{18}O$ was encountered. The experimental resolution and accuracy in absolute line positions allow for a deperturbation treatment, in which the signature of the perturbation is determined as a heterogeneous one, without having access to direct information on the perturber state. From the analysis precise values for the spectroscopic constants of the $K^1\Sigma^+$, $v = 0$ as well as the perturber state are derived. The perturber is tentatively identified as the $E'^1\Pi$, $v = 5$ state.

2. MEASUREMENTS

In Fig. 1 a high-resolution spectrum of the $K^1\Sigma^+-X^1\Sigma^+$ (0, 0) band of $^{13}C^{18}O$, recorded in the wavelength range near 97 nm, is presented. It was measured with the recently completed XUV-laser spectrometer by the method of 1 XUV + 1 UV photoionization (*5, 6*). The CO molecules were excited in a crossed laser/molecular beam setup, thus avoiding Doppler broadening. The spectral linewidth of 0.3 cm^{-1} is determined by the bandwidth of the coherent XUV radiation, which was generated by frequency tripling pulsed UV radiation from a frequency-doubled dye laser in a xenon gas jet. The transition wavenumbers of the CO lines were determined by computerized interpolation between absorption peaks of I_2 (*8*) and recorded simultaneously in the visible, yielding an absolute accuracy of 0.1 cm^{-1} in the XUV region. A ^{13}C-enriched sample of carbon monoxide (MSD, 99% atom pure ^{13}C) was used, containing about 10–20% $^{13}C^{18}O$ mixed with $^{13}C^{16}O$. No evidence of $^{13}C^{17}O$ was found. Photoionized molecules were accelerated into a time of flight mass selector with a resolution sufficient to separate masses 29 and 31. In this way XUV-excitation spectra of $^{13}C^{18}O$ and $^{13}C^{16}O$ could be recorded independently. However, at frequency positions where the more abundant $^{13}C^{16}O$ molecules have high intensity, signal "leaks through" into the mass 31 channel resulting in a somewhat contaminated $^{13}C^{18}O$ spectrum. These $^{13}C^{16}O$ features are marked with an asterisk in the spectrum of Fig. 1.

The perturbation in the $K^1\Sigma^+$, $v = 0$ state of $^{13}C^{18}O$ is clearly visible in Fig. 1. In the R-branch lines pile up at $R(7)$ and a 20 cm^{-1} wide gap between $R(7)$ and $R(8)$ is observed. Correspondingly a deviation from regularity in the P branch is found, with the $P(11)$ line in between $P(7)$ and $P(8)$ and the $P(12)$ line in between $P(8)$ and $P(9)$. Moreover, in retrospect after the deperturbation analysis, the $P(9)$ and $P(13)$ lines are found to coincide. A strong decrease of intensity is found near the local perturbation at $J = 8–9$ in the excited state. Unfortunately, in the wavelength

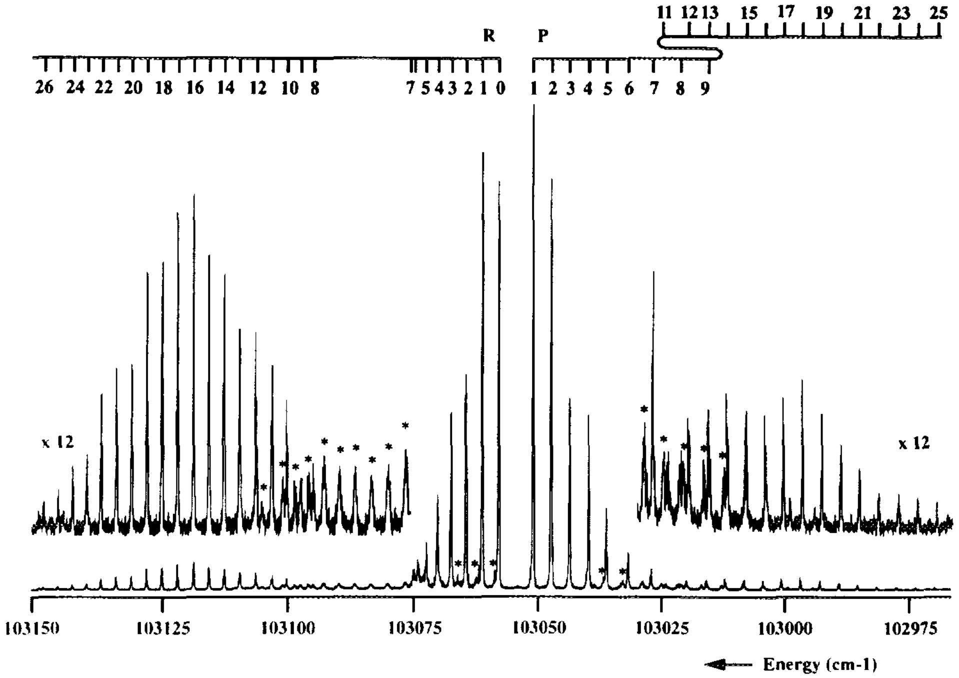

FIG. 1. Spectrum of the $K^1\Sigma^+$–$X^1\Sigma^+$ (0, 0) band of $^{13}C^{18}O$, recorded by means of 1 XUV + 1 UV mass-resolved photoionization. Lines indicated by (*) are attributed to $^{13}C^{16}O$.

regions, where the perturbation occurs (in the P and R branches), the intensity of the $^{13}C^{16}O$ lines reaches a maximum and signal leaks into the $^{13}C^{18}O$ spectrum. For this reason it was impossible to identify transitions to the perturber state which may be expected as weak resonances in this wavelength range. Also the strongly perturbed $P(10)$ line of the K–X (0, 0) band could not be identified. The rotational lines of the $K^1\Sigma^+$–$X^1\Sigma^+$ (0, 0) band of $^{13}C^{18}O$ were assigned using the method of combination differences of $P(J+1)$ and $R(J-1)$ lines. The rotational line positions, in the R branch up to $J = 27$ and in the P branch up to $J = 25$, are listed in Table I.

3. DEPERTURBATION ANALYSIS

From the gap in the R branch of the spectrum it is evident that the $K^1\Sigma^+$, $v = 0$ levels for $J \leqslant 8$ are shifted downward in energy by the interaction, while for $J \geqslant 9$ the levels are shifted upward. This local perturbation with a typical anticrossing pattern is treated phenomenologically by making use of a deperturbation method outlined by Lefebvre-Brion and Field (*1*) and by Kovacs (*9*). Actually, in Ref. (*1*) a hypothetical case of a perturbation is described and ironically the numbers found for the $K^1\Sigma^+$, $v = 0$ state closely resemble that of this example. The energies of the K state $E(K^1\Sigma^+, v = 0, J)$ and the perturber state $E_{\mathrm{pert}}(J)$ follow from diagonalizing a matrix for each J,

$$\begin{pmatrix} E(K^1\Sigma^+, v = 0, J) & H'_{\mathrm{int}} \\ H'_{\mathrm{int}} & E_{\mathrm{pert}}(J) \end{pmatrix}. \tag{1}$$

TABLE 1

Observed Rotational Line Positions of the $K^1\Sigma^+$, $v = 0$–$X^1\Sigma^+$, $v = 0$ transition of $^{13}C^{18}O$ at $\lambda = 97.04$ nm

J	R(J)			P(J)		
		Δ_{het}	Δ_{hom}		Δ_{het}	Δ_{hom}
0	103057.31	-0.10	0.23			
1	103060.60	-0.07	0.16	103050.45	-0.08	0.30
2	103063.78	-0.01	0.07	103046.85	-0.08	0.25
3	103066.74	0.03	-0.10	103043.16	-0.05	0.18
4	103069.41	0.06	-0.32	103039.36	0.01	0.10
5	103071.63	0.04	-0.56	103035.46	0.18	0.05
6	103073.21	-0.08	-0.65	103030.99	0.05	-0.32
7	103074.19	-0.13	0.12	103026.28	0.08	-0.51
8	103094.15	0.10	-1.82	103020.90	-0.02	-0.58
9	103096.55	-0.09	-0.64	103015.08	0.11	0.36
10	103099.31	-0.12	-0.04			
11	103102.27	-0.11	0.24	103023.25	-0.08	-0.64
12	103105.50	0.06	0.49	103019.14	-0.02	0.07
13	103108.75	0.19	0.61	103015.08	-0.06	0.29
14	103111.81	0.08	0.45	103011.33	0.10	0.53
15	103114.91	-0.00	0.28	103007.50	0.11	0.53
16	103118.08	-0.02	0.18	103003.56	-0.04	0.32
17	103121.38	0.10	0.21	102999.91	0.08	0.36
18	103124.53	0.08	0.11	102996.14	0.07	0.27
19	103127.61	0.03	-0.02	102992.30	-0.00	0.10
20	103130.63	-0.06	-0.16	102988.52	-0.01	0.02
21	103133.65	-0.10	-0.24	102984.72	-0.01	-0.05
22	103136.73	-0.04	-0.19	102980.89	-0.01	-0.11
23	103139.64	-0.08	-0.23	102976.92	-0.12	-0.25
24	103142.58	-0.04	-0.15	102973.05	-0.08	-0.23
25	103145.40	-0.05	-0.09	102969.18	0.01	-0.14
26	103148.24	0.04	0.10			
27	103151.04	0.16	0.37			

Note. Δ_{het} and Δ_{hom} represent deviations between observed line positions and an analysis with a heterogeneous and a homogeneous perturbation, respectively. All values are in cm^{-1}.

In case of a homogeneous interaction,

$$H'_{int} = H_{int}, \tag{2}$$

where H_{int} is a constant independent of J. In case of a heterogeneous interaction involving a $^1\Sigma$ state the J dependence for the off-diagonal matrix element (*1, 9*) is

$$H'_{int} = H_{int}\sqrt{J(J+1)}, \tag{3}$$

with H_{int} constant. The deperturbed rotational state energies of both states are represented by

$$E = \nu_0 + BJ(J+1) - DJ^2(J+1)^2. \tag{4}$$

We note that in case of a heterogeneous perturbation the perturber state will have $^1\Pi$ symmetry. As only the Π_e level will be affected, its energy may be represented as if it were a $^1\Sigma^+$ state.

Because the energy positions of the perturber states are not known, there is no simple means for determining whether the interaction parameter is J dependent or not. A priori it is clear from the sign of the energy shifts that the band origin ν_0 of the perturber state is higher and that the B constant is necessarily smaller than that of the $K^1\Sigma^+$, $v = 0$ state. In case of a heterogeneous perturbation the interaction at $J = 0$ is zero, while at the high J values, away from the anticrossing point, the interaction will not vanish. This is entirely different for the case of a homogeneous perturbation and it may seem a simple problem to decide between the two possibilities. However, the effects of energy shifts at $J = 0$ or high J may be compensated for by a different choice of the molecular constants of the perturber state and of the $K^1\Sigma^+$, $v = 0$ state itself. It turns out that a rather accurate numerical treatment is necessary to decide on the nature of the interaction.

The energies of the $K^1\Sigma^+$, $v = 0$ J states were derived by averaging over values from R and P transitions and using the $X^1\Sigma^+$, $v = 0$ ground state term energies calculated from the constants of Guelachvili *et al.* (*10*) for $^{13}C^{18}O$: $B = 1.7464083$ cm^{-1} and $D = 5.048 \times 10^{-6}$ cm^{-1}. Energies $E(K^1\Sigma^+, v = 0, J)$ were calculated in a least-squares minimization routine by varying seven parameters: three molecular constants for both states involved and a value for the interaction parameter H_{int}. This procedure was executed with the assumption of a homogeneous perturbation (Eq. (2)) as well as with a heterogeneous perturbation (Eq. (3)). The parameters obtained in both cases are listed in Table II. In case of a heterogeneous perturbation the parameters are most accurate and a standard deviation of $\sigma = 0.09$ cm^{-1} results, while with the assumption of a homogeneous perturbation $\sigma = 0.44$ cm^{-1}. These values are to be compared with the estimated experimental accuracy of 0.1 cm^{-1}. Table I also

TABLE II

Molecular Constants for the $K^1\Sigma^+$ $v = 0$ state of $^{13}C^{18}O$ and the Perturber State as Obtained in Two Different Least-Squares Fits, One Assuming a Heterogeneous Perturbation and One a Homogeneous Perturbation

	Heterogeneous	Homogeneous
$\nu_0 (K^1\Sigma^+)$	103054.02 ± 0.03	103056.66 ± 0.05
$B (K^1\Sigma^+)$	1.7477 ± 0.0002	1.7541 ± 0.0006
$D (K^1\Sigma^+)$	$1.43 \pm 0.03 \times 10^{-5}$	$2.00 \pm 0.03 \times 10^{-5}$
$\nu_{0,\text{pert}}$	103073.44 ± 0.15	103093.7 ± 0.2
B_{pert}	1.507 ± 0.002	1.24 ± 0.01
D_{pert}	$2.3 \pm 0.2 \times 10^{-5}$	$0.2 \pm 0.3 \times 10^{-5}$
H_{int}	1.018 ± 0.003	11.0 ± 0.3
σ	0.09	0.44

Note. H_{int} is the interaction parameter. σ represents the standard deviation of the fit. All values are in cm^{-1}.

includes the deviations between observed and calculated values for the transition frequencies for both models. The deperturbation analysis based on the assumption of a heterogeneous perturbation clearly gives a better fit and its standard deviation is in good agreement with the experimental accuracy.

Additional insight may be obtained from a graphical analysis. In Fig. 2 the absolute values of the level shifts $|\Delta E|$ caused by the interaction are plotted as a function of J in the same way as in Ref. (*1*) (see Fig. 4.8). For $J \leqslant 8$ ΔE is negative, but the anticrossing pattern vanishes as the absolute values of the level shifts are plotted. The abscissa, for which $\Delta E = 0$, represents energies of the $K^1\Sigma^+$, $v = 0$ J states with the parameters of Table II, but with $H_{\text{int}} = 0$. The curves represent the energies based on the constants of Table II including H_{int}. The points represent the experimental values. Even in the case of the analysis with a homogeneous perturbation the agreement still might be called satisfactory. Close inspection reveals that at $J \leqslant 2$, $J = 9$, and J around 14 deviations between theory and experiment are found. In the case of the heterogeneous perturbation nearly all data points, the size of which represent the 0.1 cm^{-1} uncertainty, fall on the theoretical curve.

A remark should be made about the intensities of the observed lines. If it is assumed that the XUV-excitation probability to the perturber state has negligible oscillator strength, rotational lines of the perturber are nevertheless expected because of intensity borrowing. At the same time the intensity of K–X lines will decrease as a result of an admixture of the dark perturber state. This qualitatively explains the drop of intensity near $J = 8$ followed by a revival for $J > 10$. Quantitatively the intensity will be proportional to $|c_K|^2$, with c_K the K state fraction following from diagonalization of the matrix in Eq. (1). The heterogeneous perturbation $|c_K|^2$ is about equal to 0.56 for both $J = 8$ and 9, while $|c_K|^2$ is 0.50 and 0.70 for $J = 8$ and 9, respectively, in the homogeneous perturbation model. At $J < 5$ and $J > 15$ the differences in the values for $|c_K|^2$ in both models are less than 10%. In view of the statistical noise on the observed intensities and because lack of knowledge on the population distribution over $^{13}C^{18}O$ rotational states in our molecular beam, we conclude that the intensity information is not sufficient for characterizing the perturbation. In both models $|c_K|^2$

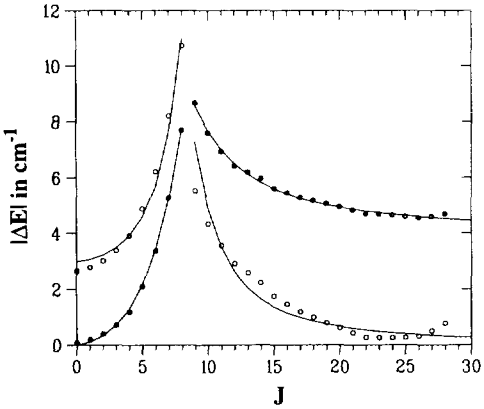

FIG. 2. Absolute values of level shifts $|\Delta E|$ as a function of J, caused by the perturbation. The abscissa, for which $\Delta E = 0$, represents the energies of $K^1\Sigma^+$, $v = 0$ J states calculated with the constants of Table II and $H_{\text{int}} = 0$. The curves represent calculated shifts, for both models, using the constants of Table II, including the value for H_{int}. Points represent differences between experimental minus the calculated value for the unperturbed case (i.e., $H_{\text{int}} = 0$): (○) homogeneous perturbation; (●) heterogeneous perturbation.

$\geqslant 0.5$ for all J, and as a consequence the intensity drop near the anticrossing should be less than 50% for all lines. The observed decrease of intensity is, however, larger than a factor of two (see Fig. 1). In 1 XUV + 1 UV photoionization the intensity is proportional to the lifetime of the intermediate state, excited by XUV radiation. We are thus led to conclude that the perturber state predissociates faster than the $K^1\Sigma^+$, $v = 0$ state.

4. DISCUSSION

The present investigation deals with an example of a strongly, but locally, perturbed vibronic state in a rare isotopomer of carbon monoxide. The example elucidates how an analysis of a perturbed state, without additional spectroscopic information on the perturber state, suffices characterizing the perturbation. A detailed numerical analysis gives insight into the accuracy required for this decision. The standard deviation of 0.44 cm^{-1} resulting from the minimization routine, using a J-independent off-diagonal matrix element representing a homogeneous perturbation, implies that if the experimental accuracy had been 0.5 cm^{-1} an unambiguous decision would not have been possible. For a general conclusion with regards to the required accuracy, the maximum energy shift, in the present case about 10 cm^{-1}, needs to be considered. From the present example one might deduce that an experimental accuracy on the percentage level of the maximum perturber-induced energy shift is required for a definite statement on its character. It is noted that the location of the perturbation in $K^1\Sigma^+$, $v = 0$ at $J = 8$–9 is fortunate for an analysis, because at both sides of the anticrossing a sufficient number of data points is available.

Having established that the perturbation in the $K^1\Sigma^+$, $v = 0$ state of $^{13}C^{18}O$ is heterogeneous, it follows that the perturber state has $^1\Pi$ electronic symmetry (*1, 9*). Furthermore, for the occurrence of an anticrossing it is necessary that the perturber is a bound state. From the observed intensity distribution it follows that the perturber is a rapidly predissociating state. In their absorption study on four different isotopomers of carbon monoxide Eidelsberg and Rostas (*11*) identified the three lowest vibrational states of the $E^1\Pi$ state of $^{13}C^{18}O$ in the energy range 92 900–97 000 cm^{-1}. The vibrational band origins of these $v = 0$–2 and that of the perturber state are plotted in Fig. 3. The band origin of the perturber state coincides with the extrapolation of the low v states and this is taken as an indication that the perturber state might be the $E^1\Pi$, $v = 5$ state. Both the $K^1\Sigma^+$ and the $E^1\Pi$ state of CO are Rydberg states converging to the $X^2\Sigma^+$ $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p)$ core of CO^+, plus a $(\sigma 4p)$ or $(\pi 3p)$ orbital. A heterogeneous perturbation by an operator of the type $(J^+L^- + J^-L^+)/2\mu R^2$ is possible for such a combination of states.

The B constants of the $E^1\Pi$, $v = 0$–2 levels vary from 1.784 to 1.736 cm^{-1}, while the rotational constant of the perturber state, now tentatively assigned as $E^1\Pi$, $v = 5$, is 1.507 cm^{-1}. From ab initio calculations of Cooper and Kirby (*12*) it follows that the $E^1\Pi$ state adiabatically correlates to the pair of ground state atoms $C(^3P) + O(^3P)$. With a potential minimum of $T_e = 11.53$ eV all rovibrational levels are found to be quasibound. Chemical bonding in the $E^1\Pi$ state is established by a potential maximum at $R = 3.2\ a_0$ of 2.18 eV above the dissociation limit and 13.71 eV above the ground state, so the $E^1\Pi$, $v = 5$ level (band origin at 12.78 eV) is still bound although a fair tunneling probability giving rise to predissociation may be present. The outward bending of the potential curve at $R > 2.5\ a_0$ will certainly cause a smaller rotational constant for the higher vibrational levels. These facts support the hypothesis that the $E^1\Pi$, $v = 5$ state acts as the perturber of the $K^1\Sigma^+$, $v = 0$ state of $^{13}C^{18}O$.

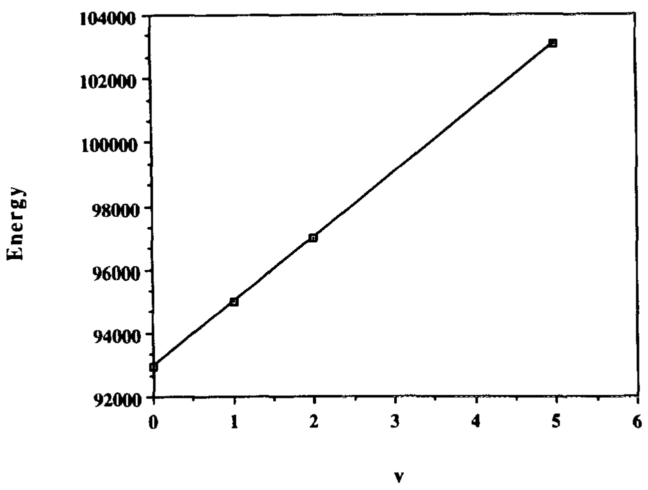

FIG. 3. Vibrational band origins ν_0 for $E^1\Pi$, v = 0–2 levels from Ref. (*2*) and the band origin of the perturber state obtained in the present analysis. An extrapolation fits assuming the perturber to be $E^1\Pi$, v = 5.

The perturbation in the $K^1\Sigma^+$, $v = 0$ state is not found in the spectra of $^{12}C^{16}O$ and $^{13}C^{16}O$ isotopomers. From extrapolation of the isotope shifts in $E^1\Pi$, v levels (*11*) the $E^1\Pi$ $v = 5$ level of $^{13}C^{16}O$ is expected to be more than 200 cm^{-1} higher in energy than the corresponding level of $^{13}C^{18}O$. The $K^1\Sigma^+$, $v = 0$ state exhibits virtually no isotope shift (<2 cm^{-1}). Therefore the location of the anticrossing in the case of $^{13}C^{16}O$ as well as $^{12}C^{16}O$ is expected at $J > 30$, in the range of states not observed.

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