

First Observation of an Identity-Forbidden Transition in Two-Photon Absorption Spectroscopy: $I^1\Sigma^- - X^1\Sigma^+$ Transition in CO

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An identity-forbidden two-photon transition has been observed for the first time, between the $I^1\Sigma^-$ and $X^1\Sigma^+$ states in carbon monoxide. Such transitions are dipole allowed only for the absorption of two photons with different frequencies and polarization states. Only P and R rotational branches of the (7-0) band are observed, and the line intensities are maximized for perpendicular photon polarizations. This is the first experimental demonstration of the two-photon electric-dipole selection rule $\Sigma^+ \rightarrow \Sigma^-$.

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The electronic states of symmetry Σ^+ and Σ^- in diatomic molecules, while both cylindrically symmetric about the internuclear axis, are distinguished by their symmetry properties with respect to reflection through any plane containing the bond axis. Electric dipole transitions between these states are rigorously forbidden by both one-photon and identical-two-photon selection rules.^{1,2} However, McClain and Harris have shown that $\Sigma^+ - \Sigma^-$ transitions become allowed for the absorption of two photons with different frequencies and polarization states, and they have called them "identity-forbidden" transitions.³

In this Letter, we report the first observation of an identity-forbidden two-photon transition, between the $I^1\Sigma^-$ and $X^1\Sigma^+$ states of carbon monoxide, using nonidentical-two-photon excitation (NTPE). This transition is characterized by a totally antisymmetric two-photon transition tensor.³ Thus the two terms in the general perturbation expression for the transition tensor S_{ab} ,

$$S_{ab} = \sum_k \left[\frac{\langle g | r_a | k \rangle \langle k | r_b | f \rangle}{\omega_{kg} - \omega_1} + \frac{\langle g | r_b | k \rangle \langle k | r_a | f \rangle}{\omega_{kg} - \omega_2} \right],$$

have opposite phases, where $|g\rangle$, $|k\rangle$, and $|f\rangle$ represent ground, intermediate, and final states: $\hbar\omega_{kg}$ is the energy between $|g\rangle$ and $|k\rangle$; $\hbar\omega_1$ and $\hbar\omega_2$ are the energies of the two photons; and r_a and r_b are components of the position vector of the electron. In the special case that $\omega_1 = \omega_2$, there is total destructive interference between these two

terms, and the tensor vanishes. For an antisymmetric tensor, the first expression simplifies to

$$S_{ab}^{\text{anti}} = (\omega_1 - \omega_2) \sum_k \frac{\langle g | r_a | k \rangle \langle k | r_b | f \rangle}{(\omega_{kg} - \omega_1)(\omega_{kg} - \omega_2)}$$

and the two-photon absorptivity is approximately proportional to the square of the frequency difference. Only Π states can contribute as intermediate states for $\Sigma^+ - \Sigma^-$ transitions, and the $A^1\Pi$ state of CO is the primary source of oscillator strength for the $I^1\Sigma^- - X^1\Sigma^+$ transition.

The $I-X$ transition in CO is excited with two ultraviolet laser sources: the fourth harmonic of a Nd:yttrium aluminum garnet (YAlG) laser at 266 nm ($\sim 0.1 \text{ cm}^{-1}$ linewidth) and a frequency-doubled Nd:YAlG-pumped dye laser at ~ 294 nm ($\sim 0.07 \text{ cm}^{-1}$ linewidth). The wave-number difference is approximately 3550 cm^{-1} in this experiment. The two beams are focused collinearly from opposite directions into a cell containing 3 Torr of carbon monoxide. Beams are focused to diameters of $70 \mu\text{m}$, with energies of 5 and 0.3 mJ at 266 and 294 nm, respectively (pulse widths of ~ 10 ns). Parallel and perpendicular linear polarization configurations are obtained by rotating a multiorder quartz half-wave plate in the path of the 266-nm beam. The $I^1\Sigma^-$ state is metastable, so that no direct fluorescence is observed. Collisional energy transfer to the $A^1\Pi$ state leads to vacuum ultraviolet fluorescence which is detected with a solar-blind photomultiplier tube.⁴ Some of the undoubled dye-laser light (~ 588 nm) is passed through an iodine fluorescence cell for wavelength calibration.

The NTPE bandhead region of the 7-0 band of the $I-X$ transition is shown in Fig. 1(a). Only P and R branches are observed, as is expected by parity considerations. Additional lines are due mainly to the $A^1\Pi-X^1\Sigma^+$ (5-0) band.⁵ Other lines are probably due to hot-band and $^{13}\text{C}^{16}\text{O}$ $A-X$ transitions.

The $I-X$ lines are distinguishable by their characteristic longer fluorescence lifetime, due to the collisional mechanism of their observation. Some of the weak, long-lifetime lines were not assignable to the $I-X$ system. These may be due to forbidden transitions to nearby triplet states.⁶ Only the $I-X$

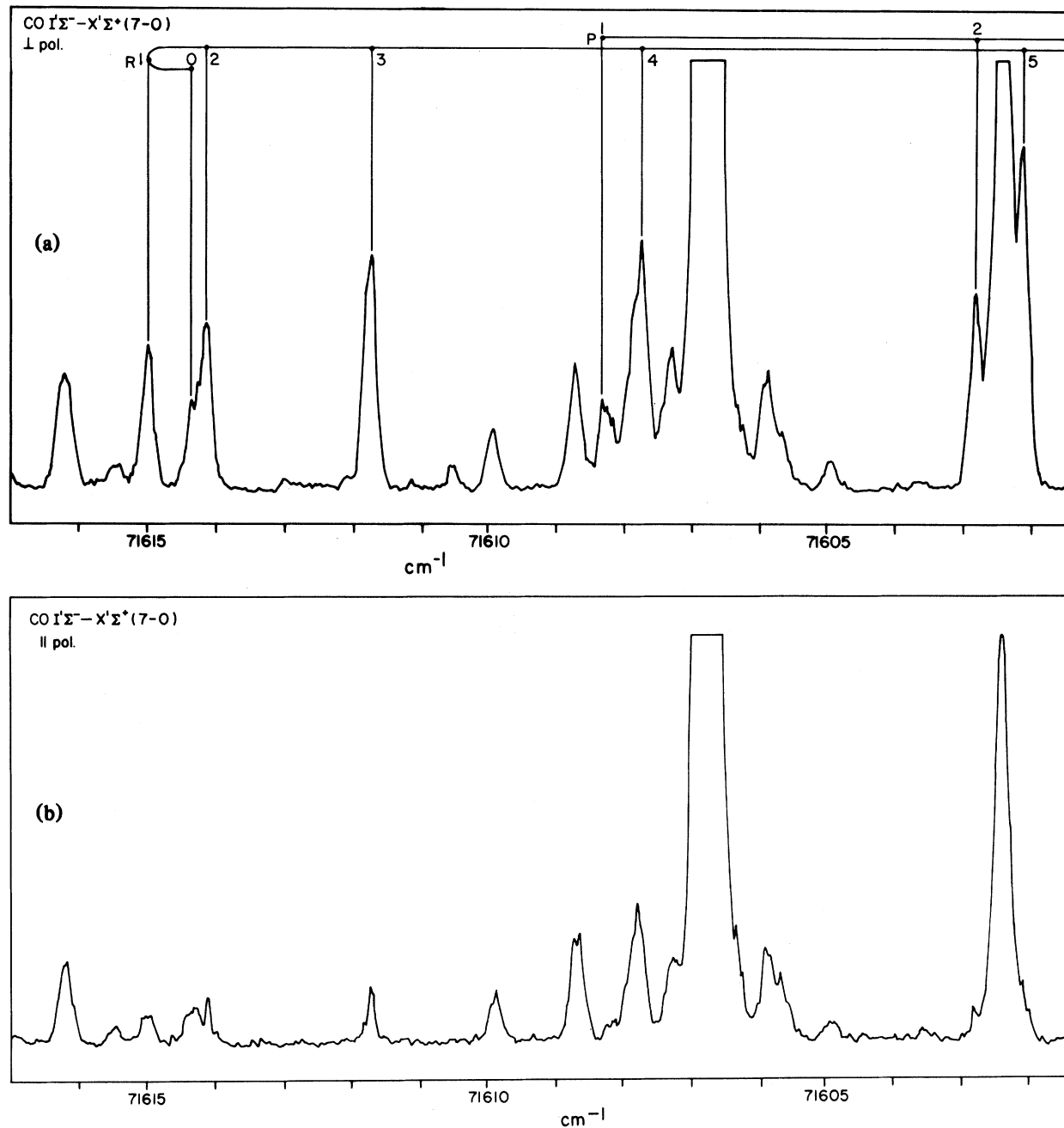


FIG. 1. NTPE spectrum of (7-0) band of the $I^1\Sigma^- - X^1\Sigma^+$ transition in CO. (a) Perpendicular polarization. P - and R -branch assignments are labeled. The two off-scale lines are, from left to right, the $P(18)$ and $R(25)$ lines of the $A^1\Pi - X^1\Sigma^+$ (5-0) band. (b) Parallel polarization. The overall signal intensity is down slightly from the scan in (a).

lines are sensitive to the polarization of the excitation sources: Their intensities are maximized with perpendicular polarization, and they nearly vanish with parallel polarization, as shown in Fig. 1(b). The line intensities are predicted to be proportional to $(1 - |\vec{e}_1 \cdot \vec{e}_2^*|)$ where \vec{e}_1 and \vec{e}_2 are the polarization vectors of the two photons.³ The observed polarization dependence is essentially consistent with this expression, and thus uniquely identifies the transition as $\Sigma^+ - \Sigma^-$. Precisely parallel polarization was probably not achieved, so that the residual intensities may be due to some residual component of orthogonal polarization. Alternatively, weak perturbations between the $I^1\Sigma^-$ and $A^1\Pi$ states may be responsible for the residual intensity. Such perturbations cannot be the major source of the $I-X$ intensities, however. $A-X$ lines are predicted³ and observed to be only mildly dependent on polarization. If A -state character had been primarily responsible for the $I-X$ intensities, the strong polarization dependence would not have been observed. Preliminary analysis yields a band origin ν_0 of $71\,612.1\text{ cm}^{-1}$ and a rotational constant B_v of 1.142 cm^{-1} .

Although forbidden according to one-photon electric dipole selection rules, the CO $I-X$ system exhibits an extremely weak one-photon absorption spectrum, attributed to rotation-electronic interaction between the I and A states.^{7,8} The bands consist of a single Q branch, with low- J lines either missing or very weak. The spectroscopic constants presented here are in good agreement with those obtained in the one-photon study, although the 7-0 band was not observed in that earlier study.

The only other attempts to observe an identity-forbidden transition ($A_{1g} - A_{2g}$) have been reported for the ${}^1B_{2u} - {}^1A_{1g}$ band system in benzene. Hampf, Neusser, and Schlag,⁹ in a two-color experiment, were unable to observe the two b_{1u} vibrations, with vibronic symmetry A_{2g} , apparently because of weak vibronic coupling.¹⁰ With use of identical-two-photon absorption, one of these vibrational modes (ν_{12}) has been observed in deuterated benzenes: by Sur, Knee, and Johnson¹¹ in sym- $C_6H_3D_3$ and by Rava *et al.*¹² in C_6H_5D . The isotopic perturbation lowers the vibrational symmetry of the molecule, and the identity-forbidden mode becomes identity-allowed, through a perturbation-induced symmetric component to the two-photon transition tensor.

In conclusion, an identity-forbidden transition has been observed for the first time. NTPE provides a means for studying a new class of symmetries (Σ^- , Σ_g^- , A_2 , A_{2g} , T_{1g}) of molecular excited electronic states; many of these states are

metastable or dark states which are likely to act as energy reservoirs in reactive systems, such as those found in atmospheric and interstellar chemistry. In addition, the production, using NTPE, of such metastable excited states as the $I^1\Sigma^-$ state of CO has possible applications in the study of gas-phase collisional processes¹³ and gas-surface interactions,¹⁴ and as intermediates in the study of higher-lying excited states.¹⁵ We are also investigating analogous identity-forbidden transitions in three-photon absorption.¹⁶

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