(33) Bonačić, V.; Koutecký, J. *J. Chem. Phys.* **1972,** *56*, 4563–4573.
(34) Shockley, W. *Phys. Rev.* **1939,** *56*, 317–323. Koutecký, J. *Adv. Chem. Phys.* **1965,** *9*, 85–168.
(35) Odell, B. G.; Hoffmann, R.; Imamura, A. *J. Chem. Soc. B* **1970,** 1675–1678. See also ref 6.
(36) The parametrization for the full CI–PPP calculations is the same as given in ref **7**. The resonance integrals for the bond which is twisted by the angle are approximated by $\beta_{ij}(\theta) = \beta_{ij}(0^0) \cos \theta$ [eV]. The electron–electron repulsion integrals γ_{ij} are calculated according to the recipe of ref 7 because the estimated difference between the values of the relevant electron–electron repulsion integrals of the type $(\pi\pi|\overline{\pi\pi})$ and $(\pi\pi|\pi\pi)$[37] is only of the order of 10%.[38] This difference is of great importance for the relative stability of the twisted conformation but only of second-order importance for the qualitative nature of the states under consideration.
(37) Roothaan, C. C. J. *J. Chem. Phys.* **1951,** *19*, 1445–1458.
(38) Hoffmann, R.; Imamura, A.; Zeiss, G. D. *J. Am. Chem. Soc.* **1967,** *89*, 5215–5220. Gondo, Y. *J. Chem. Phys.* **1964,** *41*, 3928–3938.
(39) Buenker, R. J.; Peyerimhoff, S. *Theor. Chim. Acta* **1974,** *35*, 33–58. Buenker, R. J.; Peyerimhoff, S.; Butscher, W. *Mol. Phys.* **1978,** *35*, 771–791.
(40) Bonačić-Koutecký, V.; Bruckmann, P.; Hilberty, P.; Koutecký, J.; Leforestier, C.; Salem, L. *Angew. Chem.* **1975,** *87*, 599–601. *Angew. Chem., Int. Ed. Engl.* **1975,** *14*, 575–576. Bruni, M. C.; Daudey, J. P.; Langlet, J.; Malrieu, J. P.; Momicchioli, F. *J. Am. Chem. Soc.* **1977,** *99*, 3587–3596. Brooks, B. R.; Schaefer III, H. F. *Ibid.* **1979,** *101*, 307–311. Yamaguchi, K.; Yabushita, S.; Minokawa, O.; Fueno, T. *Chem. Phys. Lett.* **1978,** *59*, 303–307. Berthier, G.; Levy, B.; Praud, L. *Gazz. Chim. Ital.* **1978,** *108*, 377–381. Meerman-van Benthem, C. M.; Jacobs, H. J. C.; Mulder, J. J. C. *Nouveau J. Chim.* **1978,** *2*, 123–127. Koutecký, J.; Bonačić-Koutecký, V.; Čížek, J.; Döhnert, D. *Int. J. Quantum Chem., Suppl.* **1978,** *12*, 357–369. Bonačić-Koutecký, V.; Buenker, R. J.; Peyerimhoff, S. *J. Am. Chem. Soc.* **1979,** *101*, 5917–5922. See also ref 13.
(41) Our conjecture of the importance of the π electrons is based besides general considerations and results summarized in Figure 5 on the following facts: STO-3G calculations of Borden and Davidson[20] show the relative positions of singlet and triplet in complete agreement with our full CI–PPP approach. The nature of the sudden polarization effect can be well understood in the PPP full CI approach.
(42) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971,** *54*, 724–728. Pople, J. A., et al. *QCPE* **1978,** *11*, 368.
(43) Bonačić-Koutecký, V.; Buenker, R. J.; Pogliani, L., results from a work in progress.
(44) Bonačić-Koutecký, V.; Sevin, A.; Döhnert, D., results from a work in progress.
(45) Döhnert, D.; Koutecký, J.; Bonačić-Koutecký, V., results from a work in progress.

Torsional Modes in the Multiphoton Ionization Spectrum of Tetrachloroethylene

Barbara A. Heath and M. B. Robin*

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974.
Received September 11, 1979

Abstract: Hyperconjugation has been identified by Mulliken as the cause of nonplanarity in the (π, 3s) Rydberg state of ethylene. This nonplanarity is signaled by the highly abnormal contributions of the torsional mode to the one-photon vibronic spectrum. The two-photon resonance to the corresponding excited state in tetrachloroethylene is observed to be much sharper than its one-photon counterpart, and vibronic analysis of it shows a near absence of torsional activity, consonant with a planar upper state and no hyperconjugative interaction. The two-photon polarization ratio as measured in the multiphoton ionization spectrum is very close to zero (<0.05), as appropriate for a totally symmetric vibronic upper state. The major intensity-inducing vibrations in the two-photon spectrum (ν_{11}' and ν_{12}') have b_{3u} symmetry, and the electronic origin is at 50 429 cm^{-1}.

Though this paper is formally focused on the tetrachloroethylene (TCE) molecule, we were prompted in this direction by a consideration of the interesting spectroscopic and geometric problems presented by ethylene, the parent molecule. Consequently, we open with a brief discussion of the transition to the lowest Rydberg state of ethylene in order to present a proper frame of reference for an evaluation of the results on TCE. The key papers on the electronic excitations in ethylene are those of Wilkinson and Mulliken[1,2] and the more recent analyses by Merer and Schoonveld[3a] and Foo and Innes.[3b] Reviews on the spectra of olefins can be found in ref 4 and 5.

The optical or electron-impact excitation of an electron from the π MO of ethylene (b_{3u}) into the lowest Rydberg orbital, 3s, displays a vibronic envelope very much like that observed in the photoelectron spectrum corresponding to ionization from the π orbital.[5] Thus it is clear that the 3s Rydberg orbital is essentially nonbonding as regards the core, and that the geometric changes are induced by the extraction of the electron from the π orbital. Removal of an electron from the π MO has two direct consequences: (a) the C–C bond order decreases, and so a progression in the C–C stretch (ν_2) is excited. This vibrational frequency decreases from 1623.3 cm^{-1} in the ground state to 1368 cm^{-1} in the (π, 3s) excited state, and simultaneously the C–C distance expands from 1.338 to 1.41 Å. (b) The decrease in C–C π-bond order on excitation dramatically decreases the force constant for torsional motion (ν_4), such that its frequency drops from 1023 cm^{-1} in the ground state of ethylene-h_4 to only 96 cm^{-1}, and from 726 cm^{-1} to only 41 cm^{-1} in ethylene-d_4.

In the (π, 3s) upper state of ethylene, the twisting potential is centered about the planar geometry (for $v_4 \geqslant 2$ in the torsional mode ν_4), and so in the electronically allowed excitation the ν_4 vibrations can appear only as changes of double quanta, i.e., $0 \rightarrow 2$, $0 \rightarrow 4$, $1 \rightarrow 3$, etc. Even though allowed by symmetry, such vibrations in general are not expected to be very intense, for, as explained by Herzberg,[6] in the usual case where a vibrational frequency ω'' of ca. 1000 cm^{-1} decreases by 20% or so upon excitation, but the potential curves are not displaced, 99.4% of the Franck–Condon intensity remains at the origin, according to the formula

$$\frac{I(0,0)}{\sum_{v} I(0, v)} = \frac{2\sqrt{\omega'\omega''}}{\omega' + \omega''}$$

In fact, in the extraordinary case of ethylene, the double-quantum excitation of ν_4' in the one-photon spectrum is quite prominent, and indeed the formula above predicts that, owing to the extreme reduction in vibrational frequency, only 56% of the intensity is found at the origin. Moreover, irregular intensities in these twisting doublets, as well as irregularities observed in their frequencies, also suggest a double minimum along the torsional coordinate in the upper state. Further experimental and theoretical analysis[7,8] confirms that in the upper level the ethylene molecule (and positive ion) is twisted by 25–30°, with a barrier height of 280 cm^{-1}.

0002-7863/80/1502-1796$01.00/0

Mulliken offers an interesting explanation.[8] Consider the $^2B_{3u}$ positive ion in the valence-bond formulation as resonating between the two forms

$$H_2{=}\dot{C}{-}C^{+}{=}H_2 \leftrightarrow H_2{=}C^{+}{-}\dot{C}{=}H_2$$

Hyperconjugation could lead to further stabilization of the ion due to structures such as

$$H_2{=}C{=}C{-}H_2^{+} \leftrightarrow H_2^{+}{-}C{=}C{=}H_2$$

except for the fact that in planar ethylene the two types of structure do not mix owing to symmetry. However, this restriction is relaxed in the twisted ion, where the competing effects of C-C π-bond order, which favors a planar structure, and C-H π-bond order (hyperconjugation), which prefers a 90°-twisted structure, equilibrate to produce a compromise dihedral angle of 30°. Since the optical electron in the (π, 3s) Rydberg state is nonbonding, the argument given above for the positive ion is applicable to the Rydberg state as well.

Recapitulating, the unusual activity of ν_4' in the (π, 3s) Rydberg state of ethylene arises from the huge decrease of torsional force constant upon excitation. In turn, this decrease is a consequence of the stabilization of the twisted configuration by hyperconjugation.

The interesting questions as to the geometric and spectroscopic situations in derivatives of ethylene have not been investigated as yet. The reason in large part is that, with the heavier substituents, the torsional frequency drops considerably, and relatively highly resolved spectra (5-10 cm^{-1}) are necessary for analysis, whereas the π→3s one-photon excitations of all substituted ethylenes[5] are orders of magnitude broader than this. We have found, however, that the two-photon resonance in TCE is sufficiently sharp for vibrational analysis. Depending upon the extent of hyperconjugation in this molecule, and focusing on the activity of ν_4 in the transition, we expect either (a) a large fractional decrease of the torsional frequency in the Rydberg state (ca. 90%), together with prominent progressions of either double quanta of ν_4 (planar upper state) or single quanta of ν_4 (twisted upper state) of high anharmonicity, or (b) a modest decrease in the torsional frequency accompanied by a relatively minor role for it in the vibronic spectrum, with little ν_4 intensity away from the origin and modest anharmonicity.

In the one-photon spectrum of TCE, Figure 1, we see that there is no hope of observing any ν_4 activity (expected to have a spacing much less than 100 cm^{-1} in the upper state). Studying this spectrum and the corresponding photoelectron band,[9] one recognizes the long progressions in C-C stretching (ν_1'), to which are added quanta of the totally symmetric C-Cl stretch (ν_2').[10,11] These latter stretches appear in the tetrahalide spectra but not in that of ethylene itself because in the former the substituent π orbitals are mixed with the C-C π MO, whereas this cannot occur in ethylene.

We turn instead to two-photon spectroscopy, as detected by three-photon ionization. In this technique, the output pulses from a nitrogen-pumped dye laser are focused into a cell containing the vapor of interest (ca. 10 Torr) and a pair of parallel-plate electrodes biased at 190 V. When the dye-laser frequency is scanned into two-photon resonance with the gas, the overall ionization cross section rises dramatically as measured with an external electrometer and the "multiphoton ionization" (MPI) spectrum, resonant at the second photon, results.[12]

In ethylene and TCE, the transition in question is π→3s ($b_{3u} \rightarrow a_g$), and is one photon allowed, two photon forbidden. In this situation we rely on vibronic allowedness to produce the two-photon spectrum. In TCE the possible intermediate states for the two-photon π→3s excitation are shown in Scheme I with the allowing vibrations shown above the arrows representing the absorption of the second photon. All three of these intermediate states followed by nine choices of u-type vibronic enhancement are a priori candidates; however, the b_{2g} intermediate seems most likely on intensity grounds, though b_{1g} (C-Cl σ*) may be energetically competitive since the π→σ* A bands are apt to be low lying.[5] Of course, any number of these paths may be operating simultaneously. With the change in selection rules, the two-photon spectrum of ethylene itself also would be of interest, but at present it is beyond our spectral range.

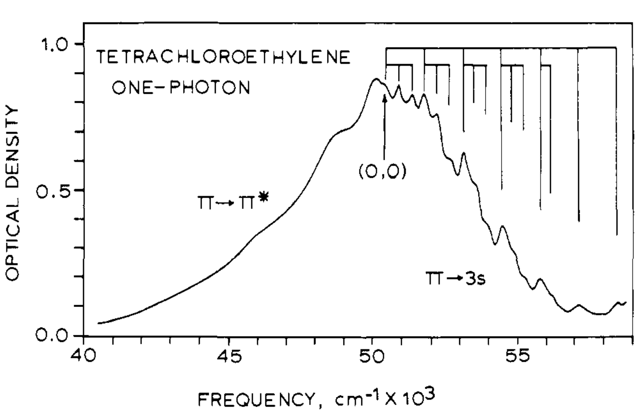
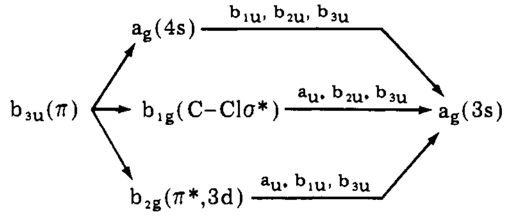


Figure 1. The one-photon absorption spectrum of TCE recorded with a spectral slit width of 30 cm^{-1}.

Scheme I



There is a striking difference between the one-photon spectrum presented in Figure 1 and the two-photon spectrum of TCE shown in Figure 2. The latter is richly structured and shows no intensity in the region of the one-photon origin (approximately 50 400 cm^{-1}). The absence of the origin is to be expected but the narrowness of the lines in the MPI spectrum is surprising considering their appearance in the one-photon spectrum. Admittedly, the spectral bandwidth of the spectrometer used to generate Figure 1 was only 30 cm^{-1}, whereas that used for Figure 2 was approximately 1 cm^{-1}. It is obvious, nonetheless, that the natural widths of the bands in the one-photon spectrum are orders of magnitude larger than those in the two-photon spectrum.

Table I lists the frequencies of the major transitions and their assignments. Not shown in Figure 1 is the region from 3750 to 3590 Å, which was broad and only very weakly structured. The intricacy of the TCE spectrum comes in part from the fact that more than one allowing vibration is present. Each serves as a false origin, being decorated with sequences, progressions, and hot bands in the totally symmetric vibrations. Thus the region 3760-3950 Å in Figure 2 appears to be the superposition of several identical spectra displaced from one another by the differences in the excited-state frequencies of the allowing vibrations.

The three-photon ionization potential wavelength of TCE is 3982 Å. At longer wavelengths, four photons are required for ionization and thus the possibility exists for one-photon ionization from a three-photon resonant state. This process is expected to be much weaker than a two-photon-resonant/one-photon ionization. We believe that the relatively broad bands which intrude on the sharp spectrum above 3982 Å are due to such a three-photon resonant state lying just below the ionization potential. Note the increased sensitivity required

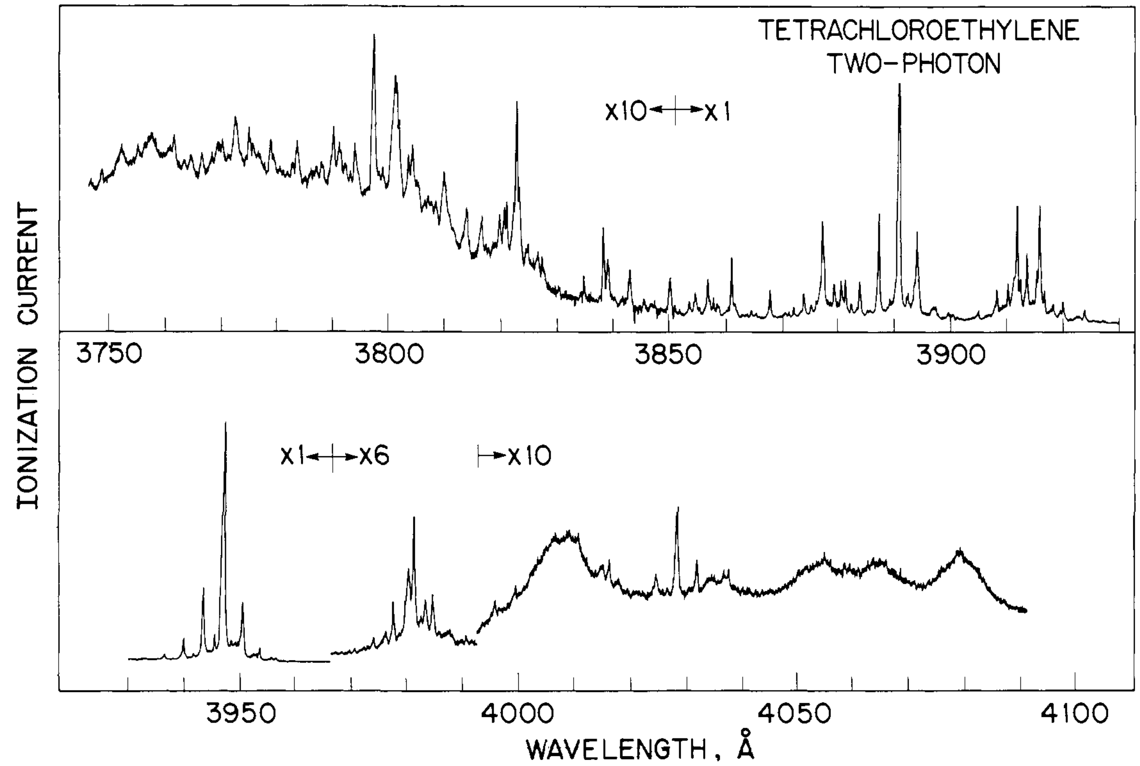


Figure 2. Intermediate resonances in the MPI spectrum of TCE, uncorrected for dye gain. The following dye solutions were used: diphenylstilbene (4090-3990 Å), PBBO (4000-3920 Å), dye 386 (3950-3780 Å), and PBD (3820-3590 Å).

to record the spectra in the region of four-photon ionization from the ground state.

The most prominent features in the two-photon spectrum of TCE are the "false origins" found at 50 670 and 51 403 cm^{-1}. They are both surrounded by a dense pattern of sequence bands, and this pattern is found accompanying every other major feature in the spectrum. Where, however, is the true origin, invisible in this case due to the two-photon selection rule? In the one-photon spectrum, there is evident a clear pattern of repeating bands: strong, weak, weak (ν_1', ν_2', ν_2') beginning with two weak, weak features (Figure 1). Extrapolation to the unresolved strong component (presumably the origin) yields a frequency of 50 350-50 380 cm^{-1}. Indeed, in the two-photon spectrum, there is a rather wide gap in this region, and furthermore the intense band at 50 670 cm^{-1} has a long progression of prominent 456-cm^{-1} intervals (ν_2') stretching from it to higher frequency, but none can be seen below. Thus, the forbidden origin must lie in the 50 300-50 600-cm^{-1} region.

The exact position of the origin is most easily determined as that point in the 50 300-50 600-cm^{-1} region from which one can identify ground-state vibrations on the low-frequency side. By trial and error, it is found that with a choice of 50 429 cm^{-1} as origin the bands at 50 247, 50 120, and 49 650 cm^{-1} then have ground-state frequencies of 182, 309, and 779 cm^{-1}, to be compared with the IR/Raman values of 177 (ν_{10}'', b_{2u} CCl_2 rock), 309 (ν_{12}'', b_{3u} CCl_2 scissors), and 777 cm^{-1} (ν_{11}'', b_{3u} CCl_2 symmetric stretch).[13,14] Note that the 50 429-cm^{-1} choice for the origin is close to the one-photon value, and that the three ground-state vibrations are of u symmetry, as predicted by the vibronic mixing scheme postulated above.

Having identified certain vibrations as vibronically active in promoting hot-band absorption, one then expects that they would be prominent as well as false origins on the other side of the true origin. Of course, other vibrations which might have too great a frequency to be appreciably populated at room temperature may fail to appear on the low-frequency side of the origin, but still may be prominent on the high-frequency side. Let us examine the two major features of the spectrum at 50 670 and 51 403 cm^{-1} with this in mind. With respect to the origin at 50 429 cm^{-1}, the band at 50 670 cm^{-1} corresponds to an allowing vibration of 241-cm^{-1} frequency, and is most reasonably assigned to ν_{12}'. With due allowance for anharmonicity, the feature at 51 103 cm^{-1} can be assigned to $3\nu_{12}'$. The alternative assignment of this band as yet another false origin seems less likely. The band observed at 51 403 cm^{-1} is displaced from the true origin by 974 cm^{-1}, and is assigned to ν_{11}', increased from the ground-state value of 777 cm^{-1}.

Having established the origin and the allowing vibrations, we can return to the subspectra associated with each allowing vibration. Note that any vibration of g symmetry added to the b_{3u} or b_{2u} false origins also leads to a vibronically allowed transition. The most prominent of these is ν_2' (a_g, CCl_2 symmetric stretch), increased from 451[15] to 457 cm^{-1} in the excited state. Harmonic progressions with as many as four quanta of ν_2' are built upon both ν_{11}' and ν_{12}'. The increase in ν_2 frequency upon excitation was also seen in the one-photon spectra.[10,11] That the vibrational frequency of the C-Cl stretch should increase upon electronic excitation follows from the nature of the π MO, which is C-Cl antibonding.

A spacing of 404 cm^{-1} is found to the high-frequency side of all of the major bands, and is assigned as ν_6' (b_{1g}, CCl_2 rock, 347 cm^{-1} in the ground state). The C-C stretch, ν_1', is a landmark feature of the one-photon Rydberg spectrum of TCE with a value of approximately 1350 cm^{-1}. In the two-photon spectrum, quanta of 1270 cm^{-1} are appended to the ν_{11}' and ν_{12}' false origins, and are assigned to ν_1'. A sparse showing of other vibrations can be assigned as in Table I.

The excitation of an electron from the b_{3u} π orbital of TCE into the 3s level combined there with a b_{3u} vibration results in a state of A_g vibronic symmetry. According to McClain, a two-photon transition to such a totally symmetric state will have a polarization ratio, Ω, less than $3/2$.[16] This quantity refers to the ratio of two-photon absorption intensities measured with circularly and linearly polarized light. On the other hand, for

Table I. Vibrational Intervals in the MPI Spectrum of Tetrachloroethylene[a]

one-photon wavelength, Å	two-photon frequency, cm^{-1}	$h\nu - 50\,429$ cm^{-1}	$h\nu - 50\,670$ cm^{-1}	$h\nu - 51\,403$ cm^{-1}	assignment
4028.2	49 650	−779			ν_{11}''
4017.7	49 780	−649			$\nu_6'' + \nu_7''$
3995.6	50 055	−374			$\nu_{11}'' + \nu_6'$
3990.4	50 120	−309			ν_{12}''
3981.3	50 235	−194			$\nu_6'' + \nu_7'' + \nu_2'$
3980.3	50 247	−182			ν_{10}''
3953.4	589		−81		$\nu_{12}' + 2\Delta\nu_4$
3950.5	626		−44		$\nu_{12}' + \Delta\nu_4$
3947.1	50 670[b]	241	0	ν_{12}	ν_{12}'
3945.5	691		21		
3943.4	718		48		$\nu_{12} + \Delta\nu_{10}$
3941.7	740		70		
3939.9	763		93		$\nu_{12}' + 2\Delta\nu_{10}$
3938.2	785		115		
3936.6	805		135		$\nu_{12}' + 3\Delta\nu_{10}$
3915.9	51 074	645	404		$\nu_{12}' + \nu_6'$
3913.7	51 103	674	433		$3\nu_{12}'$
3911.8	51 127	698	457		$\nu_{12}' + \nu_2'$
3890.8	51 403	974		0	ν_{11}'
3881.3	51 529	1100	859		$\nu_{12}' + \nu_2' + \nu_6'$
3879.4	51 554	1125	884		$3\nu_{12}' + \nu_2'$
3877.2	51 584	1155	914		$\nu_{12}' + 2\nu_2'$
3867.7	51 710	1281	1040		$\nu_{12}' +$ J[c]
3860.9	51 801	1372		398	$\nu_{11}' + \nu_6'$
3856.7	51 858	1429		455	$\nu_{11}' + \nu_2'$
3848.1	51 974	1545	1304		$\nu_{12}' + \nu_1'$
3847.3	51 985	1556	1315		$\nu_{12}' + 2\nu_2' + \nu_6'$
3842.9	52 044	1615	1374		$\nu_{12}' + 3\nu_2'$
3838.1	52 109	1680	1439		L[d]
3826.7	52 264	1835		861	$\nu_{11}' + \nu_2' + \nu_6'$
3822.7	52 319	1890		916	$\nu_{11}' + 2\nu_2'$
3820.7	52 346	1917	1676		$\nu_{12}' + \nu_1' + \nu_6'$
3813.9	52 440	2011		1037	$\nu_{11}' +$ J[c]
3809.8	52 496	2067	1826		$\nu_{12}' + \nu_1' + \nu_2'$
3808.3	52 517	2088			L[d] $+ \nu_6'$
3797.1	52 672	2243		1269	$\nu_{11}' + \nu_1'$
3793.5	52 722	2293		1319	$\nu_{11}' + 2\nu_2' + \nu_6'$
3789.6	52 776	2347		1373	$\nu_{11}' + 3\nu_2'$

[a] Listing only the major features and selected minor ones which are recurring. [b] The sequence structure indicated on this band is observed as well on all other intense features in the table, though not tabulated here. [c] J is probably a combination band of g symmetry. [d] L appears to be another false origin.

all other vibronic symmetries (as with a b_{2u} allowing vibration) the ratio is predicted to be equal to $\frac{3}{2}$.

Our measurements on the features at 50 670 and 51 403 cm^{-1} gave Ω values very close to zero ($\Omega < 0.05$), confirming their assignments as b_{3u} vibrations. The excitation of a_u, b_{1u}, or b_{2u} vibrations will yield an Ω value of $\frac{3}{2}$. Since the whole group of bands around 51 100 cm^{-1} as well as those around 50 200 cm^{-1} also showed a ratio of zero, the implication is that all vibrational bands are of b_{3u} symmetry. However, we are unable to offer a systematic assignment involving only b_{3u} and a_g vibrational modes, Table I. Note that McClain's theory is appropriate for a two-photon absorption, whereas we are measuring a three-photon current. As a further complication, recent mass-spectral work on benzene,[17] butadiene,[17] and acetaldehyde[18] has shown that the absorption from the two-photon resonant state can involve several more than the one photon necessary to reach the lowest ionization potential. If any of the many optical absorption steps following the initial two-photon absorption is not isotropic,[19] then it too will contribute to the measured polarization ratio. We presume that these are important factors in the case of TCE, and make interpretation in terms of a two-photon Ω difficult.

Sequence bands are also visible in the subspectra associated with each false origin. A slightly anharmonic sequence of four members is found with the first member shifted 48 cm^{-1} to the high-frequency side of each main band. In line with its high intensity, this sequence is assigned as involving $\Delta v = 0$ excitations in ν_{10}, which is only 180 cm^{-1} in the ground state. In addition, a weak satellite appears 22 cm^{-1} to the high-frequency side of each of the ν_{10} sequence bands. Though not visible in the one-photon $\pi \rightarrow 3s$ transition, the sequences observed here at 40 cm^{-1} to the low-frequency side of each false origin also were reported in the one-photon spectrum of the higher Rydberg levels.[10] They were tentatively assigned to the $\Delta v = 0$ sequence in ν_4, the torsional vibration. We concur with this assignment, and conclude that ν_4 has an upper-state value of 68 cm^{-1}, reduced from 108 cm^{-1} in the ground state.

There are nowhere present in the two-photon spectrum any features which could be ascribed to harmonic or anharmonic progressions in double or single quanta of a low-frequency vibration such as ν_4. If the TCE molecule remains planar in the (π, 3s) state with a reduction in the frequency of ν_4 comparable to that in ethylene, one expects to see prominent excitations in double quanta of ν_4 appended to each allowing vibration. As shown above, there should be appreciable intensity in these bands despite the fact that, for double quanta of an antisymmetric vibration, the symmetry remains the same in both the upper and lower state. Alternatively, progressions in single quanta of ν_4 should be visible if the (π, 3s) Rydberg state has a twisted conformation of large dihedral angle, since ν_4 is the vibration that would take the planar into the twisted geometry. For a dihedral angle of modest size, as in the upper state of ethylene, only the double quanta would appear, but with grossly irregular spacings. Neither type of progression is observed in TCE. Owing to the low frequency of the ν_4 torsion in the ground state (108 cm^{-1}), one *does* expect to find the $\Delta v = 0$ sequences appended to each allowing vibration, whether or not a change in geometry has taken place. Some lowering of the frequency of the torsional mode must occur with the loss of a bonding electron from the π MO. Consequently, the 40-cm^{-1} sequence in TCE is assigned to the torsional vibration (in accord with earlier work), having modest anharmonicity and a 68-cm^{-1} frequency in the (π, 3s) Rydberg state.

It is quite surprising to find that the two-photon transition observed here in TCE has such sharp features compared with the one-photon band in the same spectral region, and the possibility that the two spectral bands do not represent the same electronic transition must be considered. First, in support of a common $\pi \rightarrow 3s$ assignment for both, we do find that the origins, independently determined, are quite close: 50 429 (two photon) vs. 50 370 ± 20 cm^{-1} (one photon). Moreover, since no meaningful vibrational analysis is possible under the assumption that the false origins are real, it is clear that we are dealing with one-photon electronically allowed, two-photon vibronically allowed transitions, as predicted for $\pi \rightarrow 3s$. Two other possibilities are imaginable, but less likely. The $\pi \rightarrow \pi^*$ excitation falls in part in the spectral region under discussion; however, the one-photon spectrum shows its origin to be at 47 600 cm^{-1}.[11] Furthermore, one expects the (π,π^*) state to have virtually no resistance to ν_4 torsion, which is contrary to our analysis. Other alternatives involve the σ^* (C-Cl) MOs as terminating orbitals. In chloroalkanes such as CH_3Cl, the lowest frequency excitation is $Cl(3p\pi) \rightarrow \sigma^*(C\text{-}Cl)$.[5] Known as the A bands, these lone pair$\rightarrow \sigma^*$ transitions occur in the 50 000-60 000-cm^{-1} region generally, in agreement with the observation in TCE. However, such upper states are not bound with respect to C-Cl dissociation, and consequently the A bands *never* show vibrational structure. Finally, there is the possibility that we are observing a $\pi \rightarrow \sigma^*$ (C-Cl) excitation in TCE. Such a transition has never been identified positively in a halogenated π-electron system, and so we have no way of knowing where such a band might come. Still, such an assignment seems unlikely, for in this state one should see strong decreases of C-Cl stretching frequencies, whereas our vibronic analysis shows small to moderate increases.

The ultimate test of the two-photon band of TCE lies in its behavior when the sample is pressurized with a second gas. If the transition is to a Rydberg state as claimed, then the sharp features will broaden drastically and asymmetrically upon adding ca. 100 atm of a second inert gas, whereas for $\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, or A-band valence-shell assignments there will be no effect whatsoever.[5,18] We have attempted this measurement repeatedly, but find that at pressures of only 1-2 atm the MPI signal is decreased to zero intensity, regardless of the pressurizing gas, and long before any broadening can be expected to be seen. This effect has been seen in several other systems (but not all we have studied), and will be reported upon in the future.

Though our vibrational analysis is not perfect in all respects, it is sufficiently self-consistent to lead us to say with confidence that in the (π, 3s) state of TCE there is a "normal" reduction of the ν_4 torsional frequency and that its only activity is in the form of $\Delta v = 0$ sequences which appear largely due to the favorable Boltzmann population of the low-lying ν_4'' level. From this observation, there follow directly the conclusions that TCE has a planar (π, 3s) state, and that hyperconjugation in this state is of minor importance compared to the situation in ethylene. Apparently, the conjugative interaction between the π lone pairs on chlorine and the π MO of the C=C double bond is sufficiently intense in the planar ion so as to overcome totally the tendency to twist and thereby bring the C—Cl σ orbitals into hyperconjugative interaction with the double bond in TCE.

Acknowledgments. All previous vibrational spectroscopy on TCE has been performed in condensed phases, whereas our MPI work required gas-phase values. These were determined for us by G. Pasteur (IR), B. A. Wilson (far IR), and J. E. Griffiths and D. Distefano (Raman). We are grateful for their help in this study, and for critical comments from R. S. Mulliken.

References and Notes

(1) P. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, **23**, 1895 (1955).
(2) P. G. Wilkinson, *Can. J. Phys.*, **34**, 596 (1956).
(3) (a) A. J. Merer and L. Schoonveld, *J. Chem. Phys.*, **48**, 522 (1968); (b) P. D. Foo and K. K. Innes, *ibid.*, **60**, 4582 (1974).
(4) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).
(5) M. B. Robin, "Higher Excited States of Polyatomic Molecules", Vol. II, Academic Press, New York, 1975.
(6) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. III, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand-Reinhold, Princeton, N.J., 1966.
(7) See, for example, M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968).
(8) R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959).
(9) R. F. Lake and H. Thompson, *Proc. R. Soc. London, Ser. A*, **315**, 323 (1970).
(10) C. M. Humphries, A. D. Walsh, and P. A. Warsop, *Trans. Faraday Soc.*, **63**, (Part 3), 513 (1967).
(11) P. Dauber and M. Brith, *Chem. Phys.*, 11, 143 (1975).
(12) P. M. Johnson, *J. Chem. Phys.*, **64**, 4638 (1976).
(13) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies", Consolidated Vol. I, National Bureau of Standards, Washington, D.C., 1972, p 39.
(14) W. J. Schmidt and H. W. Schrötter, *Chem. Phys. Lett.*, **45**, 502 (1977).
(15) Unpublished measurement on TCE in the gas phase.
(16) W. M. McClain and R. A. Harris in "Excited States", Vol. III, E. C. Lim, Ed., Academic Press, New York, 1977, p 1.
(17) L. Zandee and R. B. Bernstein, *J. Chem. Phys.*, **71**, 1359 (1979).
(18) G. J. Fisanick, T. S. Eichelberger, IV, B. A. Heath, and M. B. Robin, *J. Chem. Phys.*, submitted for publication.
(19) J. O. Berg, D. H. Parker, and M. A. El-Sayed, *J. Chem. Phys.*, **68**, 5661 (1978).