

process.¹⁵ This result implies that the product ion must be formed with appreciable kinetic energy,¹¹ and it is consistent with an expected¹⁶ nontetrahedral geometry for $\text{Fe}(\text{CO})_4^-$.¹⁷

The $\text{Fe}(\text{CO})_3^-$ can itself photodissociate to yield $\text{Fe}(\text{CO})_2^-$ (Figure 2). The average maximum $\text{Fe}(\text{CO})_2^-$: $\text{Fe}(\text{CO})_3^-$ intensity ratio was 3%. No photoproduction of $\text{Fe}(\text{CO})_2^-$ occurs if $\text{Fe}(\text{CO})_3^-$ is continuously ejected; the cross section is unaffected if $\text{Fe}(\text{CO})_4^-$ is ejected. Filter studies confirm that the disappearance of $\text{Fe}(\text{CO})_3^-$, with $\text{Fe}(\text{CO})_4^-$ being partially ejected, parallels the appearance of $\text{Fe}(\text{CO})_2^-$; signal/noise considerations prevented monochromator data for the disappearance of $\text{Fe}(\text{CO})_3^-$ from being taken.

In accord with previous work,¹² we find that $\text{Fe}(\text{CO})_3^-$ appears to be more reactive than $\text{Fe}(\text{CO})_4^-$. For example, $\text{Fe}(\text{CO})_3^-$ condenses with $\text{Fe}(\text{CO})_5$ to give $\text{Fe}_2(\text{CO})_6^-$; increases in $\text{Fe}_2(\text{CO})_6^-$ (due to newly formed $\text{Fe}(\text{CO})_3^-$) were observed upon irradiation with light. In the presence of SF_6 the usual photodissociation curve for $\text{Fe}(\text{CO})_4^-$ was observed but no $\text{Fe}(\text{CO})_3^-$ was detected. Instead, new ions corresponding to $\text{Fe}(\text{CO})_2\text{F}_2^-$, $\text{Fe}(\text{CO})_2\text{F}^-$, and $\text{Fe}(\text{CO})_2\text{F}_2^-$ were detected upon irradiation with light. Further investigations of the chemistry of $\text{Fe}(\text{CO})_3^-$ are planned.

Acknowledgments. We thank Robert G. Komoto and Professor Richard Zare for helpful discussions and John V. Garcia for technical assistance. This work was supported by the National Science Foundation (GP-37044-X) and the Center for Materials Research, Stanford University.

(15) Because the potentials on the side (trapping) plates are greater than those on the top and bottom (analyzer) plates, it is easier to lose product ions from the cell when they are ejected preferentially in the vertical direction. The disappearance of reactant has no orientational dependence; thus the effect cannot be a result of anisotropic distribution of reactant ions in the cell or anisotropic photon flux. Consequently, we can associate a preferential direction of dissociation with a specific orientation of the optical E vector.

(16) Expected, since if tetrahedral, $\text{Fe}(\text{CO})_4^-$ would undergo Jahn-Teller distortion. $\text{Fe}(\text{CO})_4^{2-}$ is tetrahedral: W. F. Edgell, *et al.*, *J. Amer. Chem. Soc.*, **87**, 3080 (1965); H. Stammreich, *et al.*, *J. Chem. Phys.*, **32**, 1482 (1960). $\text{Fe}(\text{CO})_4$ is not tetrahedral: M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1351 (1973).

(17) A tetrahedral molecule would be expected to show no anisotropy: For example, see C. Jonah, *J. Chem. Phys.*, **55**, 1915 (1971); R. N. Zare, *Mol. Photochem.*, **4**, 1 (1972); G. E. Busch and K. R. Wilson, *J. Chem. Phys.*, **56**, 3638 (1972).

(18) National Science Foundation Predoctoral Fellow.

(19) Camille and Henry Dryfus Foundation Teacher-Scholar.

Jeffery H. Richardson,¹⁸ L. M. Stephenson,¹⁹ John I. Brauman*
Department of Chemistry, Stanford University
Stanford, California 94305
Received February 13, 1974

A Novel Ion-Molecule Reaction Involving Cleavage of the Carbonyl Bond in Ketones and Aldehydes¹

Sir:

In this communication we report a unique type of reaction which we have observed between CF_3^+ , C_2F_5^+ , or CCl_3^+ and a series of organic compounds containing a carbonyl functional group. Observation of this reaction is one of the early results of a series of experiments we have initiated in which the reactions of halo-

(1) This work was partially supported by the U. S. Atomic Energy Commission.

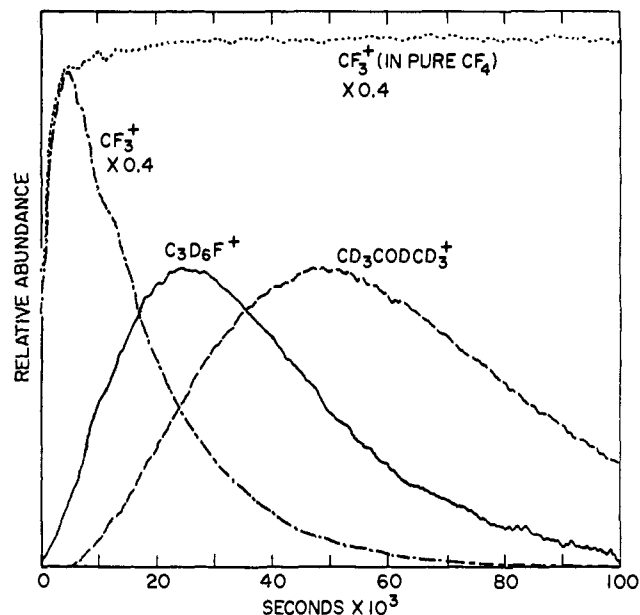


Figure 1. Relative abundances of ions formed in a CF_4 - CD_3 - COCD_3 (1:0.028) mixture as a function of time at a total pressure of 7.0×10^{-6} Torr and the abundance of CF_3^+ in the absence of additives under the same conditions. The $\text{CD}_3\text{CODCD}_3^+$ ion disappears because of further reaction with CD_3COCD_3 to form the $(\text{CD}_3\text{COCD}_3)_2\text{D}^+$ ion.

carbon ions with various types of organic molecules are investigated.²

All experiments were carried out in a pulsed ion cyclotron resonance (icr) mass spectrometer^{2,3} in which relative abundances of reactant and product ions can be followed as a function of time after an initial ion formation pulse several milliseconds in duration. Mixtures containing 2-5% of a carbonyl compound in CF_4 , C_2F_6 , or CCl_4 were admitted to the icr instrument at pressures of 10^{-6} - 10^{-5} Torr. In these compounds, a pulse of 40 eV electrons results in the formation of CF_3^+ (in CF_4), CF_3^+ and C_2F_5^+ (in C_2F_6), and CCl_3^+ (in CCl_4) as the predominant primary ions;⁴ these ions are all unreactive with the respective parent compounds (see Figure 1). The observed decay of parent ions and growth of product ions as a function of time gave information about reaction mechanisms and allowed determination of reaction rate constants with an accuracy of $\pm 10\%$. In addition, all product ions were unambiguously traced to their particular precursor ion(s) through use of the technique of icr double resonance ejection.⁵

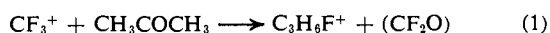
(2) J. R. Eyler, P. Ausloos, and S. G. Lias, to be submitted for publication.

(3) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971).

(4) When CF_4 , C_2F_6 , or CCl_4 are admitted to the instrument in the absence of additives, small fragment ions such as CF_2^+ (in CF_4) or CCl_2^+ (in CCl_4) are formed initially along with the reactant ions of interest. However, these smaller ions react rapidly with the respective parent compounds, and in the pressure range used in these experiments are essentially absent after about $5-10 \times 10^{-3}$ sec. It should be pointed out that the use of high dilution mixtures for the investigation of these reactions (a technique similar to that called "chemical ionization mass spectrometry") not only allows us to ignore possible interactions with minor fragment ions but also ensures that the reactant ions undergo a sufficient number of unreactive collisions that those ions which react have attained thermal energies. This conclusion is supported by the fact that changes in mixture composition or pressure have no effect on the rates or modes of reaction observed.

(5) W. T. Huntress, Jr., and R. F. Pinizzotto, Jr., *J. Chem. Phys.*, **59**, 4742 (1973).

The major reaction between CF_3^+ or CCl_3^+ and most aldehydes and ketones, $\text{R}'\text{COR}$, results in the cleavage of the carbonyl bond and the formation of a monohalogenated product ion, $\text{R}'\text{CXR}^+$ (in which X is F or Cl). For example, CF_3^+ and CCl_3^+ react with acetone to give respectively $\text{C}_3\text{H}_6\text{F}^+$ and $\text{C}_3\text{H}_6\text{Cl}^+$ (eq 1 and 2)



as major product ions. In a mixture of C_2F_6 and acetone, no new product ions appeared, and a double resonance experiment demonstrated that, in this case, $\text{C}_3\text{H}_6\text{F}^+$ product ions are formed in a reaction of C_2F_5^+ (3) as well as in reaction 1. An analogous product ion



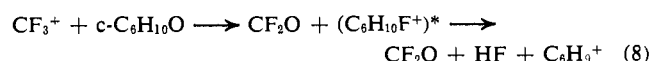
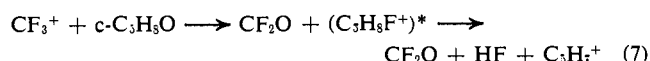
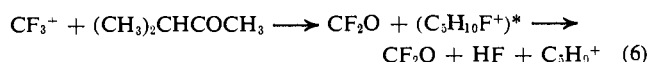
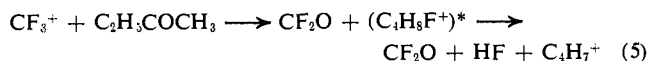
is also formed in the reaction between CF_3^+ and acetaldehyde (eq 4). (Because the masses of these ions



could not unambiguously be attributed to the $\text{C}_3\text{H}_6\text{F}^+$ or $\text{C}_2\text{H}_4\text{F}^+$ ions, these product ions were distinguished from possible oxygen-containing ions of the same mass in experiments in which fully deuterated acetone or acetaldehyde were used in the respective mixtures.)

In reactions 1–4, the neutral products have been written assuming that the reaction proceeds through some concerted mechanism in which a reciprocal exchange of an O atom and F^+ or Cl^+ occurs. These reactions could also be envisioned as proceeding through an initial transfer of F^+ or Cl^+ to the carbonyl compound, followed by loss of an O atom from the excited product ion. However, it can be estimated⁶ that the reaction of CF_3^+ , CCl_3^+ , or C_2F_5^+ with acetone to form $\text{C}_3\text{H}_6\text{X}^+$ with O and CF_2 , CCl_2 , or C_2F_4 as neutral products would be at least 4.8, 6.2, or 3.8 eV endothermic, respectively, while the reaction of CF_3^+ with acetaldehyde giving O and CF_2 as neutral products would be at least 4.1 eV endothermic. On the other hand, reactions 1–4, as written, can be estimated to be ca. 1.3–2.4 eV exothermic,⁶ as shown in Table I.

When larger ketones are allowed to react with CF_3^+ , the monofluorinated carbonium ions homologous to that formed in reaction 1 are not observed. Instead, the major product ions are usually the ions corresponding to the loss of HF from the monofluorinated ions.



(It is interesting that the $\text{C}_5\text{H}_8\text{F}^+$ ion formed in a reaction between C_2F_5^+ and cyclopentanone analogous to reaction 7 does not undergo dissociation.) Loss of HF from the monofluorinated product ion is not completely

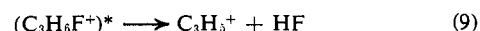
(6) Thermodynamic data are obtained or estimated from the following sources: (a) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. Field, NSRDS-NBS-26 (1969); (b) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London and New York, 1970; (c) E. Domalski, private communication.

Table I. Rate Constants and Estimated Enthalpies of Reaction of CF_3^+ , CCl_3^+ , and C_2F_5^+ with Carbonyl Compounds

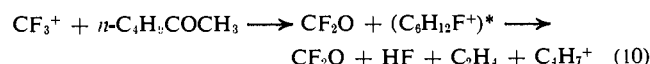
| Reactant pair | $\text{cm}^3/(\text{molecule sec}) \times 10^9$ | | Reaction no. | Estimated ⁶ ΔH , eV |
|---|---|---|--------------|--|
| | Exptl k_{RN} (total) | Estimated ⁷ $k_{\text{collision}}$ | | |
| $\text{CF}_3^+ + \text{CH}_3\text{CHO}$ | 1.25 | 2.1 | (4) | -1.7 ± 0.3 |
| $+ \text{CH}_3\text{COCH}_3$ | 2.2 | 2.1 | (1) | -2.4 ± 0.3 |
| $+ \text{C}_2\text{H}_5\text{COCH}_3$ | n.d. | n.d. | (5) | -2.5 ± 0.3 |
| $+ (\text{CH}_3)_2\text{CHCOCH}_3$ | 2.4 | 2.0 | (6) | -2.7 ± 0.4 |
| $+ \text{c-C}_3\text{H}_5\text{O}$ | 3.1 | n.d. | (7) | -2.6 ± 0.4 |
| $+ \text{c-C}_6\text{H}_{10}\text{O}$ | 2.7 | n.d. | (8) | -3.1 ± 0.4 |
| $+ n\text{-C}_4\text{H}_9\text{COCH}_3$ | n.d. | n.d. | (10) | -2.7 ± 0.4 |
| $+ \text{CH}_3\text{COOCD}_3$ | 1.4 | 1.5 | (12) | |
| $\text{C}_2\text{F}_5^+ + \text{CH}_3\text{COCH}_3$ | 1.7 | 1.9 | (3) | -2.2 ± 0.3^a |
| $+ \text{c-C}_3\text{H}_5\text{O}$ | 2.9 | n.d. | | -2.5 ± 0.3^a |
| $\text{CCl}_3^+ + \text{CH}_3\text{COCH}_3$ | 0.03 | 2.1 | (2) | -1.3 ± 0.4 |
| $+ \text{C}_2\text{H}_5\text{COCH}_3$ | 0.14 | 1.7 | | -1.4 ± 0.4 |
| $+ n\text{-C}_4\text{H}_9\text{COCH}_3$ | 0.25 | | | -1.6 ± 0.4 |

^a Assuming $\text{C}_2\text{F}_4\text{O} = \text{CF}_3\text{CFO}$.

absent in the reaction between CF_3^+ and acetone (reaction 1). In fact at a pressure of 7×10^{-6} Torr, about 30% of the product $\text{C}_3\text{H}_6\text{F}^+$ ions of reaction 1 undergo the analogous dissociation.



When $n\text{-C}_4\text{H}_9\text{COCH}_3$ was added to CF_4 , neither the monofluorinated carbonium ion nor the expected $\text{C}_6\text{H}_{11}^+$ fragment ion was observed. Rather, the major ion resulting from the $\text{CF}_3^+ - \text{C}_4\text{H}_9\text{COCH}_3$ reaction was C_4H_7^+ , which would result if the $\text{C}_6\text{H}_{11}^+$ ion underwent a further dissociation to lose ethylene. The decreased



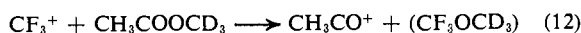
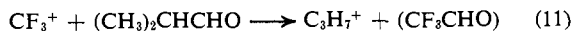
stabilities of the monofluorinated product ions of these reactions may reflect the fact that the dissociation reactions are much more exothermic for the larger ketone molecules. While further dissociation of the product ions of reactions 1–4 would lead to overall reactions exothermic by 0.4–1.7 eV, the overall reactions 5–8 are exothermic by 1.9–3.0 eV.

It can be estimated⁶ that the reactions of CCl_3^+ with these carbonyl compounds are approximately 1.1 eV less exothermic than the corresponding reactions of CF_3^+ . This is reflected in a greater stability of the monohalogenated product ions. For instance, in the reaction of CCl_3^+ with $\text{C}_2\text{H}_5\text{COCH}_3$, the major product ion is $\text{C}_2\text{H}_5\text{CClCH}_3^+$, and only 10% of these ions undergo further dissociation ($\Delta H_{\text{overall}} \sim -1.0$ eV) to give $(\text{C}_4\text{H}_7^+ + \text{HCl})$ at a pressure of about 6×10^{-6} Torr. In the reaction with $\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$ about 65% of the product $\text{C}_2\text{H}_5\text{CClC}_2\text{H}_5^+$ ions lose HCl ($\Delta H_{\text{overall}} \sim -1.6$ eV), and in the reaction with $n\text{-C}_4\text{H}_9\text{COCH}_3$ essentially all of the monochlorinated product ions lose HCl to give $\text{C}_6\text{H}_{11}^+$ as the major product ion ($\Delta H_{\text{overall}} \sim -2.6$ eV).

It is interesting that the rate constants of the reactions of CF_3^+ and C_2F_5^+ with carbonyl compounds all lie in the range $1\text{--}3 \times 10^{-9}$ while the less exothermic reactions of CCl_3^+ exhibit much lower rate constants (Table I). In a few cases, the rate constants for collision for some of these ion-molecule pairs have been estimated using the average dipole estimation method

of Su and Bowers.⁷ The measured rate constants for reactions of CF_3^+ or C_2F_5^+ with acetone $(\text{CH}_3)_2\text{CHCOCH}_3$ and $\text{CH}_3\text{COOCD}_3$ are very close to the estimated collision rate constants. If we accept these values for the collision rate constants, we must conclude that these reactions of CF_3^+ and C_2F_5^+ are very efficient, while the CCl_3^+ ion has a relatively low probability that a collision with these molecules will lead to reaction.

For all the ion-molecule reaction pairs listed above, with the exception of $\text{CF}_3^+(\text{CH}_3)_2\text{CHCOCH}_3$, other reaction channels constituted 5% or less of the total reaction. However, not all carbonyl compounds undergo reactions involving cleavage of the $\text{C}=\text{O}$ bond to the exclusion of other reaction channels with these ions. When the carbonyl compound contains a weak bond, displacement reactions compete effectively. For instance, at least 95% of the reaction between CF_3^+ and $(\text{CH}_3)_2\text{CHCHO}$ or $\text{CH}_3\text{COOCD}_3$ proceeds as follows.



A similar reaction mechanism occurs between CF_3^+ and $(\text{CH}_3)_2\text{CHCOCH}_3$ where about 20% of the product ions are C_3H_7^+ .

In reactions of C_2F_5^+ with higher ketones, CF_3CO^+ was an important product ion.

In every mixture, product ions further reacted with the carbonyl compound to form the protonated ketone or aldehyde as the final ionic product (Figure 1).

(7) T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 347 (1973).

(8) NRC-NBS Postdoctoral Research Associate.

J. R. Eyler,⁸ P. Ausloos, S. G. Lias*

National Bureau of Standards, Radiation Chemistry Section
Washington, D. C. 20234

Received January 29, 1974

Structural Implication in Metalloporphyrins of the 1590- cm^{-1} Anomously Polarized Resonance Raman Line¹

Sir:

A number of studies²⁻⁶ have demonstrated the utility of resonance Raman spectroscopy as a structural probe of the chromophore in heme proteins. Correlations between both the frequencies and the intensities of the fundamental vibrations seen in the resonance spectrum and the spin or oxidation state of the iron have been noted. By examining a series of metalloporphyrins, we have observed that the appearance of an anomalously polarized line in the 1582-1609- cm^{-1} spectral region reliably indicates that the metal resides in-plane with the porphyrin moiety. For this line, neither the metal oxidation nor its spin state is of primary im-

(1) This work was supported by grants from the National Institutes of Health (AM-14344 and GM-18894), the National Science Foundation (GP-17061), and the Research Corporation.

(2) T. G. Spiro and T. C. Strekas, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2622 (1972).

(3) T. Yamamoto, G. Palmer, D. Gill, I. T. Salmeen, and L. Rimai, *J. Biol. Chem.*, **284**, 5211 (1973).

(4) D. W. Collins, D. B. Fitchen, and A. Lewis, *J. Chem. Phys.*, **59**, 5714 (1973).

(5) L. A. Nafe, M. Pezolet, and W. L. Peticolas, *Chem. Phys. Lett.*, **20**, 563 (1973).

(6) T. M. Loehr and J. S. Loehr, *Biochem. Biophys. Res. Commun.*, **55**, 218 (1973).

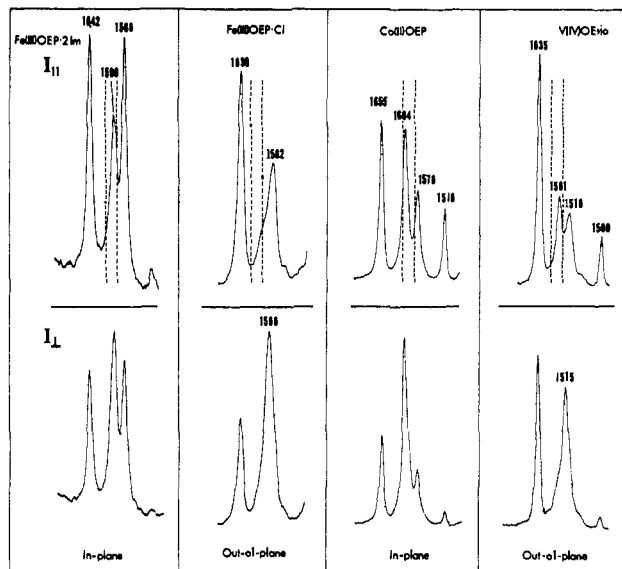


Figure 1. Parallel and perpendicular components of the resonance Raman spectra of metalloporphyrins in KBr (excited with 514.5-nm radiation). Orientation of the pellet is 10° from the incident beam. Accidental degeneracy is manifested in the frequency shift observed between $I_{||}$ and I_{\perp} in FeOEP·Cl and VOEtio.

portance. An independent observation⁷ that the resonance Raman spectrum contains geometrical information recently has been advanced by Spiro and Strekas.

Synthetic metalloctaethylporphyrin (MOEP) or -etioporphyrin I (MEtio) were chosen because of the similarity of their resonance Raman spectra to those of the heme proteins. Spectra were obtained with 0.5-1 mM solutions of the porphyrin dissolved in CH_2Cl_2 , in KBr pellets (1 mg porphyrin/200 mg KBr),⁸ or as a crystalline powder affixed to transparent tape. A rotating cell or platform was used to prevent photodecomposition of the chromophore during laser irradiation. Exciting wavelengths were 457.9, 488.0, and 514.5 nm (argon ion laser) and 560.0, 570.0, and 580.0 nm (tunable dye laser).

The differences observed between the solid and solution sample spectra were limited to anomalous polarization ratios ($\rho = I_{\perp}/I_{||} > 0.75$) that were two to three times smaller in the solid samples. This effect was not found for the polarized or depolarized bands, nor was there an appreciable shift in the vibrational frequencies for any of the lines when spectra of the solid and solution samples were compared.

Upon irradiation at 514.5 nm an anomalously polarized line (ap) was found (group I) at 1609 cm^{-1} in Ni^{II} Etio, 1604 cm^{-1} in Co^{II} OEP, 1598 cm^{-1} in Co^{III} OEP·Imid(OH), 1590 cm^{-1} in Fe^{II} OEP·2Imid, and 1587 cm^{-1} in Cu^{II} OEP. With the same experimental conditions a polarized line ($\rho < 0.75$) was seen (group II) at 1592 cm^{-1} in iron(III) protoporphyrin IX dimethyl ester, 1591 cm^{-1} in $(\text{Fe}^{\text{III}}$ OEP)₂O, 1591 cm^{-1} in V^{IV} OEtio, 1591 cm^{-1} in Zn^{II} OEP, 1584 cm^{-1} (shoulder) in Fe^{III} OEP·Cl, and 1583 cm^{-1} in Mg^{II} OEP. Representative spectra are shown in Figure 1. Comparison of the members of group I with those of group II demonstrates that neither spin nor valence state of the metal correlates with the appearance of the anomalously

(7) T. G. Spiro and T. C. Strekas, *J. Amer. Chem. Soc.*, **96**, 338 (1974).

(8) K. N. Solovoyov, N. M. Ksenofontova, S. F. Shkirman, and T. F. Kachura, *Spectrosc. Lett.*, **6**, 455 (1973).