Empirical methods for determination of ionization gauge relative sensitivities for different gases

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The relative sensitivities of a Bayard–Alpert ionization gauge for various organic molecules have been measured. There is a good correlation with total ionization cross section at 75 eV. For monofunctional compounds a correlation with number of electrons is seen with different functional groups on different lines. The best general correlation is with the polarizability, α, with $R_x = 0.36\alpha + 0.30$, where R_x is the chemical sensitivity relative to $N_2 = 1.00$. Alkanes and the noble gases have slightly larger R_x values than predicted by this equation.

Introduction

Ionization gauges, such as the Bayard–Alpert gauge[1], are widely used as pressure measuring devices in the 10^{-3}–10^{-11} torr range, due to their reliability, linearity over a wide pressure range and negligible electronic calibration needs. Their principle drawback is their selective response to different gases: sensitivity may vary by a factor of 30 for helium compared to large organic molecules. Most ion gauges are calibrated to read true pressure for nitrogen, with smaller molecules in general giving readings lower than the true pressure and larger ones higher than true readings. The chemical sensitivity of an ion gauge for some compound X, S_x, is defined as the ratio of the observed pressure divided by the true pressure. It is well established that the absolute chemical sensitivity of an ion gauge for a given gas can vary by more than 30% depending on the design and condition of the gauge tube, and its operating parameters[2]. Thus, any attempt to compile standard absolute chemical sensitivities for various gases from a variety of sources will not provide useful data, unless all values are related to some common compound. The ratio of chemical sensitivities for two different compounds, however, appears to be much more constant[2,3]. Summers has shown that the ratio of the chemical sensitivities for compound X relative to that for nitrogen, $R_x = S_x/S_{N_2}$, varies by only 7% for widely different gauges and operating conditions[3]. There have been published several tables of such relative sensitivities, R_x, for small inorganic molecules[2-11], as well as for hydrocarbons[12] and a limited number of more complicated organic compounds[3,13].

Recent advances in the measurement of ion–molecule reactions have created a need for such chemical sensitivities for a wide variety of organic compounds. Absolute chemical sensitivities are needed for the determination of rate constants in low pressure devices such as ion cyclotron resonance (ICR) spectrometers, since it is accurate absolute pressure determination that is the principal source of uncertainty in such work. Relative ion gauge chemical sensitivities are used in the measurement of equilibrium constants, such as for proton, electron and hydride transfer[14]. In ICR spectrometry, common practice is to perform such experiments while measuring the pressure using an ion gauge, then afterwards to calibrate the ion gauge for each gas used. This is done by measuring the pressure of each pure gas in the 10^{-5}–10^{-4} torr region using both the ion gauge and some absolute pressure measuring device such as a capacitance manometer. It would be of considerable use to have some method for predicting the ion gauge chemical sensitivity for any compound, both to facilitate the proper setting of experimental pressures and to obtain values for compounds too nonvolatile or unstable to calibrate against the capacitance manometer in the normal way. There have been proposed several such correlations of chemical sensitivities with molecular properties such as with number of electrons[4,12,15], number of valence electrons weighted by orbital radii[16], total ionization cross section at various energies[3,13] and polarizability[3]. Most of these correlations have used compilations of ion gauge sensitivity values for different compounds from a variety of literature sources. Considering the variation in absolute chemical sensitivities that arise from minor changes in ion gauge construction and operating conditions and the general lack of data for most organic functional groups, we have undertaken the determination of ion gauge chemical sensitivities for a wide range of compounds under constant laboratory conditions.

Experimental

The vacuum system used in this work is that of the ICR spectrometer at Indiana University. It consists of a $110\,l\,s^{-1}$ turbomolecular pump joined through a throttle value to a 1 m long by 6.2 cm internal diameter manifold. Gases are admitted at the far end through a leak valve and the pumping speed is

regulated by the throttle valve to be *ca* 4 l s^{-1} at the ion gauge. The ion gauge (Huntington Mechanical Labs inverted Bayard–Alpert IK-150 gauge tube with a Thoria coated iridium filament using a Granville–Phillips Model 270 Controller) and the capacitance manometer (MKS Baratron Model 146 head) are mounted on short 3 cm internal diameter side arms halfway down the manifold on either side of it. The capacitance manometer is set on a 90° elbow to remove it from line of sight of the ion gauge filament, since, when formerly mounted directly opposite each other, the pressure registered by the capacitance manometer would drift for 30 min following degassing of the ion gauge. If the manometer is mounted at the end of a 50 cm by 1 cm dia tube off the manifold, as is common in many ICR spectrometers[17], the ion gauge sensitivity factor for all compounds is found to vary with the numbers of turns that the throttle valve is open. Using standard formulas[2], the pumping speed at the ion gauge in such a configuration is estimated to be *ca* 30 times that at the capacitance manometer. The present symmetrical configuration of the two devices gives sensitivities independent of the throttle valve opening.

The organic compounds used in this work were purified by preparative gas chromatography, distillation or recrystallization. Careful purification is necessary since small amounts of more volatile impurities can greatly increase the apparent sensitivity. The ion gauge was degassed and allowed to cool for at least 15 min before each run, with the background pressure at less than 5 x 10^{-7} torr. The compound to be measured was admitted to the system and readings of both the ion gauge and capacitance manometer pressures taken at several stable pressures in the 1–10 x 10^{-5} torr range. A plot of ion gauge (abscissa) vs capacitance manometer (ordinate) pressures gave a line with slope equal to the absolute chemical sensitivity and intercept zero. Any run with correlation coefficient $r < 0.999$ or intercept negative or greater than 1 x 10^{-6} torr, due to capacitance manometer drift, was discarded. Since absolute chemical sensitivities were observed to vary up to 20% from day to day, either nitrogen or acetone was also measured each day and the ratio S_x/S_{N_2} or $S_x/S_{acetone}$ was taken as the relative sensitivity factor. All relative chemical sensitivities were then scaled to $S_{N_2} = 1.0$ or $S_{acetone} = 2.5$. The nitrogen value is the nominal true chemical sensitivity of the ion gauge (the actual values for nitrogen were found to average to it). The acetone value, relative to nitrogen, was the average of many runs. We find that relative chemical sensitivities obtained in this manner vary less than 8% from day to day, consistent with other literature reports[3].

Results and discussion

The experimental R_x factors are given in Table 1, along with other literature values as well as a variety of molecular properties. The data of Nakao[13], a compilation of literature R_x values for small inorganics and hydrocarbons, agree with the present data reasonably well but have higher values for benzene, toluene and cyclohexane. The compilation of Summers[3] also agrees with our R_x values for inorganics and most hydrocarbons. Both of these references use data from a variety of sources and from several different types of ion gauges.

As mentioned in the Introduction, one of the goals of this work is to devise a method for predicting relative sensitivities for any compound, without having to measure either it or some homolog. Many workers have concluded that the best predictor of R_x values

Table 1. Relative sensitivities of ion gauge response, with some physical properties

Compound	R_x*	Z†	α‡	OS§	R_x‖	R_x¶
Helium	0.20	2	0.20	0.69	0.19	0.18
Neon	0.33	10	0.40	1.75	0.33	0.30
Argon	1.32	18	1.66	10.90	1.37	1.30
Krypton	1.92	36	2.54	17.40	1.91	1.90
Xenon	2.78	54	4.15	24.10	2.79	2.90
Water	0.97	10	1.47	5.29	1.25	1.10
Ammonia	1.12	10	2.26	6.84	1.11	1.23
Oxygen	0.87	16	1.60	6.58	0.87	1.0
Nitrogen	(1.00)	14	1.94	7.68	(1.00)	(1.00)
Hydrogen sulfide	1.82	18	3.78	14.80	2.20	
Carbon dioxide	1.30	22	2.65	10.74	1.36	1.4
Nitrous oxide	1.20	22	3.00	10.97	1.66	
Hydrogen	0.44	2	0.79	2.0	0.44	0.46
Methane	1.62	10	2.60	8.16	1.49	1.4
Ethane	2.84	18	4.44	14.32	2.53	2.6
Propane	2.92	26	6.30	20.48	3.80	4.2
Butane	4.46	34	8.14	26.64	4.37	
Pentane	5.21	42	9.98	32.80		4.9
Hexane	5.90	50	11.83	38.96	6.6	
Heptane	6.94	58	13.68	45.12	7.6	
Isooctane	7.21	66	15.52	51.28		
Propene	2.92	24	6.07	18.48	3.16	
Hexene	5.81	48	11.60	36.96		
Cyclohexane	5.39	48	11.08	36.96	6.4	
Cyclohexene	4.78	46	10.83	34.96	6.37	
1,3-Cyclohexadiene	4.31	44	10.63	32.96		
Benzene	4.29	42	10.40	30.96	5.18	
Toluene	5.56	50	12.31	37.12	6.81	
Ethylbenzene	5.98	58	14.18	43.28		
Cumene	6.44	66	16.03	49.44		
o-Xylene	5.43	58	14.09	43.28		
Mesitylene	5.95	66	15.94	49.44		
Methanol	1.69	18	3.28	11.45		
Ethanol	2.04	26	5.12	17.61		
n-Propyl alcohol	2.60	34	6.95	23.77		
i-Propyl alcohol	2.86	34	6.99	23.77		
n-Butyl alcohol	3.05	42	8.79	29.93		
i-Butyl alcohol	3.13	42	8.79	29.93		
t-Butyl alcohol	3.20	42	8.79	29.93		
Neopentyl alcohol	3.96	50	10.63	36.09		
Trifluoroethanol	2.27	50	5.07	20.16		
Ethylene glycol	2.40	34	5.85	20.90		
Diethyl ether	4.03	42	8.92	29.93		
Dipropyl ether	5.25	58	12.59	42.25		
Tetrahydrofuran	3.29	40	8.06	27.93		
1,4-Dioxane	3.50	48	8.60	31.22		
Anisole	4.30	58	13.04	40.41		
1,2-Dimethoxyethane	4.40	50	9.58	17.61		
Acetonitrile	1.99	22	4.42	14.29		
Propionitrile	2.61	30	6.27	20.45		
Isobutyronitrile	3.33	38	8.11	26.60		
Acetaldehyde	1.95	24	4.57	15.61		
Acetone	2.50	32	6.41	21.77		
Butanone	3.18	40	8.20	27.93		
Hexafluoroacetone	2.59	80	6.62	26.87		
Acetic acid	1.54	32	5.26	18.90		
Methyl formate	2.02	32	4.50	18.90		
Ethyl formate	2.72	40	7.07	25.06		
Methyl acetate	3.05	40	7.07	25.06		
Ethyl acetate	3.22	48	8.22	31.22		

Table 1—*continued*

Compound	R_x*	Z†	α‡	OS§	R_x‖	R_x¶
Neopentyl acetate	5.00	72	15.42	49.70		
Trifluoroethyl acetate	2.66	72	8.71	29.60		
Methyl isobutyrate	3.91	56	10.72	37.38		
Methylene chloride	2.82	42	7.40	29.76		
Chloroform	3.34	58	8.48	40.56		
Carbon tetrachloride	3.74	74	10.49	51.36		
1,2-Dichloroethane	3.40	50	8.33	35.92		
1,1,2,2-Tetrachloroethane	4.44	82	12.12	57.52		
Tetrachloroethylene	4.53	80	12.01	55.52		
Chlorobenzene	4.88	58	12.35	42.76		
Methanethiol	2.36	26	5.62	20.96		
Ethanethiol	3.47	34	7.47	27.12		
1-Propanethiol	3.68	42	9.32	33.28		
2-Methyl-2-propanethiol	4.63	50	11.16	39.44		

* Relative to $N_2 = 1.00$.
† Total number of electrons.
‡ Polarizability, Å^3, from the method of ref 20.
§ The Otvos and Stevenson function, ref 16, being the sum of atomic valence electrons weighted by the mean square radius.
‖ Relative sensitivities, ref 13.
¶ Relative sensitivities, ref 3.

is the total ionization cross section, either at 70 eV or at the peak cross section[2,3,11,13].

Since ion gauges operate by measuring total ion current at *ca* 150 volts electron energy[2], this is a reasonable correlation. Unfortunately, total ionization cross sections are not generally available at any energy for most organic compounds other than the simplest ones. For 22 of the compounds in Table 1 for which peak total ionization cross sections are available[24], we find $R_x = 0.940\sigma_i + 0.050$, $r = 0.968$. The total ionization cross section at 70 eV is available for 27 of the compounds[24], giving $R_x = 0.815\sigma_i + 0.305$, $r = 0.961$. Due to the lack of a large data base, we thus turn to other predictors of R_x.

A correlation of R_x with the number of electrons, Z, present in a molecule was proposed by Dushman[2,6], quantified by Schutze and Stork[15], and further elaborated on by others[12,13]. In the present work, such correlations show good linearity for hydrocarbons and for the inert gases, although on lines of different slope. The common inorganic gases follow a general trend with number of electrons, but with much scatter. Our data are plotted vs number of electrons in Figure 1. For homologous series for a given functional group, linear correlations are observed. Different functional groups fall on different lines, however, with a consistent trend for smaller slope as the number of lone pairs in the molecule increases. Thus, for isoelectronic species, an amine appears to always have a smaller R_x value than does the corresponding alkane, and an alcohol has a smaller R_x value than an amine. The effect is not additive with number of electrons, as shown by the linear regression coefficients in Table 2 for a variety of functional groups. Structural isomers with the same number of lone pairs, such as ethers and alcohols, lie on different lines. Data for other functional group pairs are not extensive, but it appears that compounds with a terminal heteroatom have smaller R_x values than do isomers with the heteroatom in an internal position. Halogenated compounds, both for chloro- and fluoro-substituents, consistently fall on the low side of the trend. It also appears that for a given monofunctional compound, the R_x values
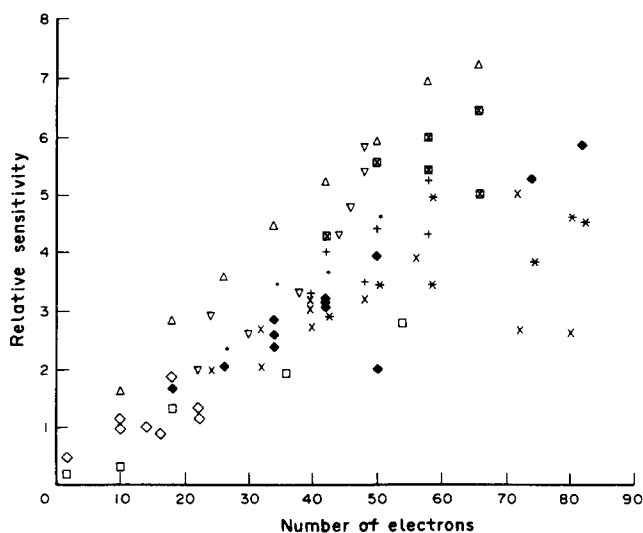

Figure 1. Relative ion gauge sensitivities vs number of electrons. ◇, small inorganics; □, noble gases; △, alkanes; ▽, alkenes, ⊠, aromatics; ◆, alcohols; +, ethers; ×, carbonyl compounds; ∗, chlorocarbons; ●, thiols. Data from Table 1.

Table 2. Correlation of relative sensitivities with number of electrons for monofunctional compounds

Function*	N†	Slope‡	Intercept‡	r§
Alkanes	8	0.100 ± 0.004	0.909 ± 0.175	0.9949
Noble gases	5	0.047 ± 0.006	0.40 ± 0.28	0.9759
Aromatics	6	0.050 ± 0.031	2.6 ± 1.8	0.6263
Alcohols	9	0.067 ± 0.003	0.346 ± 0.123	0.9923
Ethers	6	0.071 ± 0.029	0.635 ± 1.45	0.7720
Carbonyl	9	0.051 ± 0.008	0.83 ± 0.38	0.9152
Chlorocarbons	10	0.038 ± 0.007	1.282 ± 0.435	0.9444
Thiols	5	0.088 ± 0.015	0.201 ± 0.579	0.9726
Nitriles	3	0.084 ± 0.002	0.131 ± 0.041	0.9991

* From Table 1.
† Number of compounds of that class.
‡ R_x = Slope ∗ Z + Intercept, where Z = total number of electrons; uncertainties are 1 standard deviation.
§ Correlation coefficient.

can be adequately predicted from the number of electrons, but as a general correlation for all molecules this method gives too much scatter to be useful.

Otvos and Stevenson[16] have proposed that ionization cross sections be correlated with the sum of the number of valence electrons weighted by their mean square radius and have presented an atom additivity scheme for prediction of ionization cross sections. In the abstract to their work, they mention that this scheme should also be useful for relative chemical sensitivities for ion gauges, but do not further elaborate on that point in the paper. We find a correlation of our R_x values with the scheme they present, but with considerable scatter. There is some pattern to the scatter: alkanes (△) exhibit a steeper slope than for other compounds, while chlorocarbons (∗) lie below the general trend in Figure 2. Excluding these two classes, we find $R_x = 0.056 \times OS + 0.563$ ($r = 0.853$), where OS is the sum of the atomic cross section factors from the scheme presented in the Otvos and Stevenson paper[16]. Part of the apparent spread of points in the higher sensitivity region is attributable to the
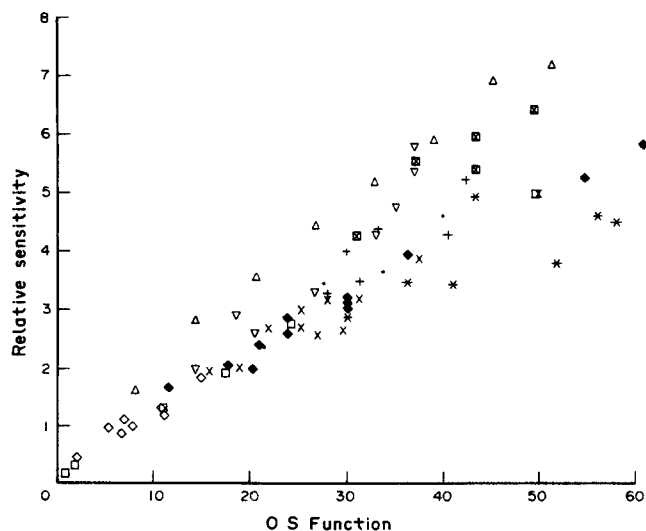
Figure 2. Relative ion gauge sensitivities vs the Otvos and Stevenson function (see text). Data from Table 1. Symbols as in Figure 1.

uncertainty in each value. Each point on the plot represents the slope of a series of points. For a constant instrumental uncertainty, such as the noise in the capacitance manometer readings, error propagation predicts a constant percent uncertainty in the R_x value. This results in much larger error bars for those compounds of higher sensitivity. The observed scatter in Figure 2 is slightly outside of this. Other workers have noted that the proposed additivity scheme does not correlate well with other ionization cross section data in the literature[18].

Beran and Kevan[19] have shown that ionization cross sections can be related to a compound's magnetic susceptibility, χ_m. As might be expected for the cases where such data is available, our R_x values do correlate with diamagnetic susceptibility reasonably well, but the lack of values for χ_m prevent general usefulness of this method.

Lampe, Franklin and Field[18] have shown total ionization cross sections for molecules to be linearly related to polarizability. Since R_x values are known to correlate with the total ionization cross section, it is not surprising that they parallel the polarizabilities as well[3]. Figure 3 shows our relative sensitivities plotted against
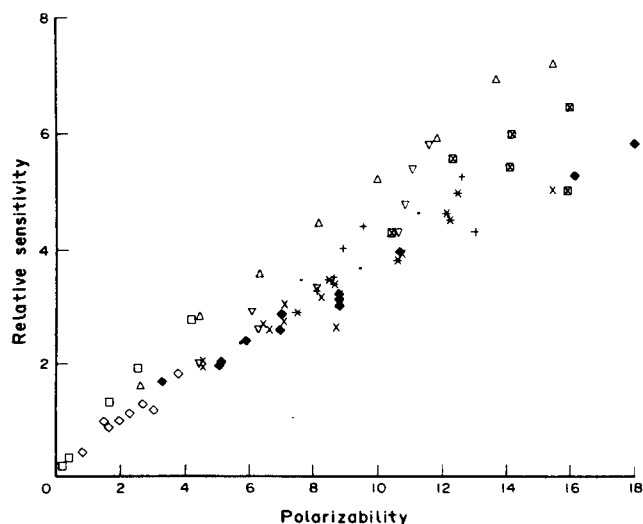

Figure 3. Relative ion gauge sensitivities vs polarizability. Data from Table. Symbols as in Figure 1.

polarizability, α. The polarizabilities are in units of cubic Angstroms and are obtained from the method of Savchik and Miller[20]. As with the correlation with mean electron radius, hydrocarbons are above the general trend for other functional groups, with $R_x = 0.50\alpha - 0.05$, $r = 0.963$. The noble gases are likewise relatively sensitive, with $R_x = 0.63\alpha + 0.22$, $r = 0.995$. For the remaining compounds, $R_x = 0.36\alpha + 0.30$, $r = 0.991$.

In other attempted correlations, little pattern is seen when the data are plotted vs thermal collision rate constants or cross sections[21] and ionization potentials[22]. There is a weak correlation ($r = 0.81$) with the $\frac{2}{3}$ power of molecular weight, but the same scatter pattern is seen when molecular weight is plotted against ionization cross sections or polarizability.

It is also interesting to note the trends for alkyl substituted benzene rings. Relative sensitivities increase in the order benzene < toluene < ethylbenzene < cumene, consistent with all predictors here, but decrease for increasing number of substituents: toluene > xylene > mesitylene. We have no explanation for the latter trend.

Is there any theoretical basis for the correlations of R_x with the various molecular properties seen here? The energy range involved is considerably higher than thermal, so the various ion-molecule collision theories pertaining to thermal species would not be expected to be suitable[21]. The Bethe theory for the collision of fast charged particles with neutral species is well developed[25] but is strictly characterized only for incident ions with velocities much greater than the orbital electron velocities. While we do not expect such a theory to exactly describe our results due to the intermediate energy range in the experiments, nevertheless it should be instructive to examine it in terms of general trends. Lampe, Franklin and Field[18] propose that the observed relationship of the total ionization cross section to polarizability is determined by the presence of the dipole moment matrix element in expressions for both the polarizability and the atomic ionization cross section. The expression for the total collision cross section is given in equation $(1)^{26}$ where M_{tot}^2 is the square of the dipole matrix elements of the molecule, c_{tot} is an incoherent scattering term, E is the incident electron energy, γ_{tot} is the contribution from quadrupole excitations, O denotes other higher orders terms and A is some constant.

$$\sigma_{tot} = \frac{A}{E}\left[M_{tot}^2 \ln(c_{tot}E) + \gamma_{tot}/E + O(1/E^2)\right]. \tag{1}$$

This equation can be reduced to equation (2) using the sum rules in ref 25, assuming a constant energy range. Z is the number of electrons in the molecule.

$$\sigma_{tot} = \frac{A'}{E}\left[a_1 Z + a_2\alpha + J_1 - J_2 + O(1/E^2)\right]. \tag{2}$$

The other terms in (2) are not necessarily independent of molecular parameters and the total cross section is only an upper limit for the ionization cross section, but the nature of the leading terms does provide a rationalization for the form of the empirical equations derived in this paper for correlating R_x with α and Z. Fitting the data to a dual substituent parameter equation in α and Z results in the best correlation having a negligible contribution from the Z term. This is mathematically consistent with the fact that Z and α are not independent functions ($r = 0.77$ for the compounds in Table 1).

In conclusion, we believe that the best method of estimating R_x values for organic compounds is the correlation with ionization

cross sections at 70 eV, $R_x = 0.815\sigma_i + 0.305$, if such data are available. The next best is the equations in Table 2, based on Z, for monofunctional organic compounds. For more general cases, the polarizability correlation $R_x = 0.36\alpha + 0.30$ is more likely to give good relative values.

Acknowledgements

References

[1] R T Bayard and D Alpert, *Rev Sci Instrum*, **21**, 571 (1950).
[2] S Dushman, *Scientific Foundations of Vacuum Technique*, 2nd edn, pp 301–350. Wiley, New York (1962).
[3] R L Summers, *NASA Tech Note D-5285* (1969).
[4] C G Found and S Dushman, *Phys Rev*, **23**, 734 (1924).
[5] N B Reynolds, *Physics*, **1**, 182 (1931).
[6] S Dushman and J R Young, *Phys Rev*, **68**, 278 (1954).
[7] S Wagener and C B Johnson, *J Sci Instrum*, **28**, 278 (1951).
[8] G J Schulz, *J Appl Phys*, **28**, 1149 (1957).

[9] H U Anderson, *Rev Sci Instrum*, **34**, 703 (1963).
[10] N G Utterback and T Griffith, *Rev Sci Instrum*, **37**, 866 (1966).
[11] R Holanda, *J Vac Sci Tech*, **10**, 1133 (1973; K Nakayama and H Jojo, *Jap J Appl Phys*, **Suppl 2**, 113 (1974).
[12] J R Young, *J Vac Sci Tech*, **10**, 212 (1973).
[13] F Nakao, *Vacuum*, **25**, 431 (1975).
[14] (a) J E Bartmess and R T McIver, Jr,*Gas Phase Ion Chemistry*. (Edited by M T Bower), Chapter 11. Academic Press, New York; (b) D H Aue and M T Bowers, ibid, Chapter 9; (c) L J Rains, H W Moore and R T McIver, Jr, *J Chem Phys*, **68**, 3309 (1978).
[15] H J Schütze and F Stork, *Vakuum Teknik*, **11**, 133 (1962).
[16] J W Otvos and D P Stevenson, *J Am Chem Soc*, **78**, 546 (1956).
[17] R T McIver, Jr, *Rev Sci Instrum*, **41**, 555 (1970); **49**, 111 (1978).
[18] F W Lampe, J F Franklin and F H Field, *J Am Chem Soc*, **79**, 6129 (1957).
[19] J A Beran and L Kevan, *J Phys Chem*, **73**, 3866 (1969).
[20] K J Savchik and J A Miller, *J Am Chem Soc*, **101**, 7206 (1979).
[21] (a) T Su and M T Bowers, *J Chem Phys*, **58**, 3027 (1973); (b) T Su and M T Bowers, *Int J Mass Spectrom Ion Phys*, **12**, 347 (1973); (c) T Su, E C F Su and M T Bowers, *J Chem Phys*, **69**, 2243 (1978).
[22] H M Rosenstock, K Draxl, B W Steiner and J F Herron, *J Phys Chem Ref Data*, **6**, Suppl 1 (1977); however, see ref 23.
[23] N Boelrijk and W H Hamill, *J Am Chem Soc*, **84**, 730 (1962).
[24] Ref 3 and references therein.
[25] M Inokuti, *Rev Mod Phys*, **43**, 297 (1971).
[26] Ref 25, equation 4.41.
[27] S Ehrenson, R T C Brownlee and R W Taft, *Prog Phys Org Chem*, **10**, 1 (1973).