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A modification to the theories of Herbst and Bates for ion–molecule association rate coefficients is presented that gives a simple formula for calculating the temperature dependence of these reactions. The present theory is compared to phase space theory and yields similar results. The modified theory is applied to several experimental systems and excellent agreement is found between experiment and theory. It is shown that a temperature dependent stabilization step is necessary to explain the experimental results in He buffers.

INTRODUCTION

The field of ion–molecule association reactions has been particularly active recently. There has been a large number of both theoretical[1–20] and experimental[15–41] papers on the subject emphasizing different aspects of the problem. In fact, the association of N_2^+ to N_2 has been the subject of at least ten papers.[11,17,30,31,33,37–41]

In its simplest form, the mechanism for ion–molecule association reactions is

$$A^\pm + B \xrightarrow{k_1} (A^\pm B)^*, \tag{1}$$

$$(A^\pm B)^* \xrightarrow{k_2} A^\pm + B, \tag{2}$$

$$(A^\pm B)^* + M \xrightarrow{k_3} AB^\pm + M, \tag{3}$$

$$(A^\pm B)^* \xrightarrow{k_4} AB^\pm + h\nu, \tag{4}$$

where the * stands for a complex with energy above the dissociation energy and M is an inert third body. The possibility of radiative stabilization is given by step 4. In reality, each step should include the possibility of state to state transitions. The above mechanism gives the general properties of association reactions: a low pressure limit ($k_2 \gg k_3[M]$ or k_4), a high pressure limit ($k_2 \ll k_3[M]$ or k_4) and an intermediate falloff region ($k_2 \approx k_3[M]$ or k_4). Inclusion of state-to-state transitions results in a more gradual change between low and high pressure kinetics than given by the above mechanism.

One particularly interesting and active aspect of the subject of ion–molecule association reactions has been the measurement of the temperature dependences of the rate coefficients of these reactions in the low pressure limit and the comparison of these to theory. In the low pressure limit, the overall association rate coefficient is given by

$$k_0 = (k_1/k_2)k_{stab}, \tag{5}$$

where k_{stab} is $k_3[M]$ or k_4 depending on whether stabilization is collisional or radiative.

There are several problems in measuring k_0 and comparing the measurements to theory. The first involves the experimental problem of ensuring that the system is in the low pressure limit. In the absence of radiative association, this can be checked by studying the reaction over as large a pressure range as possible. In this case, the zero pressure intercept of a plot of the second order rate coefficient ($k(2) = k/[M]$) vs pressure has a value of zero. The involvement of radiative association [reaction (4)] complicates this check since this leads to a nonzero intercept even in the limit of low pressure.

The second problem involves the temperature dependence of the stabilization step. This is difficult to calculate[4,8,14] and has usually been assumed to be small or negligible and has been shown to vary with the identity of the stabilizing third body (see below).

Finally, there is the temperature dependence of the ratio (k_1/k_2). As will be shown below, this constitutes the major component of the temperature dependence. For small molecules at low temperatures ($h\nu \gg kT$, where ν is the lowest frequency vibration of the reactants) Herbst[3] and Bates[8] have given a simple formula for the temperature dependence of this ratio as $T^{-l/2}$, where l is the total number of rotational degrees of freedom of the reactants. Other theories[11–20] treat low frequency vibrations but are more difficult to use. The purpose of this paper is to give a simple formula for predicting the temperature dependence of k_1/k_2 in the low pressure limit for systems for which vibrations of the reactants are active. As a corollary to this, it will be shown that information on the temperature dependence of the stabilization step can be obtained.

ANALYSIS

The ratio k_1/k_2 in the low pressure limit is given by

$$k_1/k_2 = K(T) = Q(A^\pm B)^*/[Q(A^\pm)Q(B)], \tag{6}$$

where $K(T)$ is the equilibrium constant between reactants and the excited complex and Q stands for the total partition function. After factoring the translational partition functions out of the above expression, one obtains,

$$K(T) = h^3/(2\pi\mu kT)^{3/2}{}^*q_{int}(A^\pm B)^*/$$

$$[q_{int}(A^\pm)q_{int}(B)], \tag{7}$$

where q_{int} stands for the internal partition function only and μ is the reduced mass of the reactants. The only unknown is the internal partition function of the excited complex, since the internal partition functions of the reactants can be obtained from standard statistical mechanics formulas. Herbst[3] and Bates[8] have evaluated the temperature dependence of this partition function by different means, and both have found that for a nonlinear complex

$$q_{int}(A^{\pm}B)^{*} \propto T^{+3/2}. \qquad (8)$$

This cancels the temperature dependence of the translational partition functions. The zero point vibrational energy term of the vibrational partition function has been included in the above calculations. The temperature dependence of Eq. (7) is then given by

$$K(T) \propto 1/[q_{int}(A^{\pm})q_{int}(B)]. \qquad (9)$$

In order to obtain a simple formula, Herbst[3] and Bates[8] made the restriction that $h\nu \gg kT$ to obtain the well known formula

$$K(T) \propto T^{-l/2}, \qquad (10)$$

where l is the total number of rotational degrees of freedom in the reactants. This is a consequence of the fact that at temperatures above a few degrees Kelvin rotational degrees of freedom can be treated classically (with the exception of H_2 and D_2 which have large rotational frequencies).

The temperature dependence of the rate coefficient for association in the low pressure limit is given by Herbst[3] and Bates[8] as

$$k_0 \propto T^{-(l/2 + \delta)}, \qquad (11)$$

where δ represents the temperature dependence of the stabilization step, usually assumed to be small.

For many systems this formula has given good results,[11,17,30,31,33] but systems have been studied recently in which the restriction that $h\nu \gg kT$ is not valid. It is straightforward to include the vibrational partition functions into the above expressions. Including vibration the temperature dependence of the ratio defined in Eq. (6) is given as

$$K(T) \propto T^{l/2}\Pi_i[1 - \exp(-h\nu_i/kT)], \qquad (12)$$

where the product is over all the vibrational frequencies of the reactants. For each frequency for which $h\nu \ll kT$, $K(T)$ is proportional to T^{-1}. For frequencies for which $h\nu \approx kT$, the temperature dependence of $K(T)$ will be augmented by a factor between T^0 and T^{-1}. With this addition, the temperature dependence of the rate coefficient for association reactions in the low pressure limit is given as

$$k_0 \propto T^{-(l/2 + \delta)}\Pi_i[1 - \exp(-h\nu_i/kT)], \qquad (13)$$

where again δ represents the temperature dependence of the stabilization step. Equation (13) neglects the effects of internal rotations and the possibility of low lying electronic states which will be important in some systems. These effects can also be included in a similarly straightforward manner. Patrick and Golden[14] have pointed out that for a linear complex Eq. (13) would become

$$k_0 \propto T^{-(l/2 + 1/2 + \delta)}\Pi_i[1 - \exp(-h\nu_i/kT). \qquad (14)$$

The extra factor of 1/2 arises from the absence of one rotational degree of freedom in the linear complex.

Phase space theory[15–20] has also been used extensively to model ion molecule association reactions. It is shown below that in the low pressure limit the present formulation (that involves no adjustable parameters) yields a parametric dependence on temperature similar to that predicted from phase space theory.

No attempt has been made to calculate the absolute value of the rate coefficients in this paper.

DISCUSSION

The effects of vibration on the temperature dependence of three-body association rate coefficients can be seen in comparing the association of NO_3^- and HCl[21] with that of HSO_4^- and HCl.[22] Both of these would be predicted to show a $T^{-2.5}$ temperature dependence using Eq. (10) (i.e., when vibrations have not been included). However, Viggiano et al.[22] noted that the temperature dependence of HSO_4^- clustering to HCl was $T^{-1/2}$ more negative than that for NO_3^- clustering to HCl. Even though the overall temperature dependence was larger when these ions had a HNO_3 ligand attached, this factor of $T^{-1/2}$ was still observed.[22] The factor of $T^{-1/2}$ can easily be accounted for by including vibrations. Figure 1 shows the experimental results for these systems in a nitrogen buffer, the least-squares fits to T^{-n} dependences
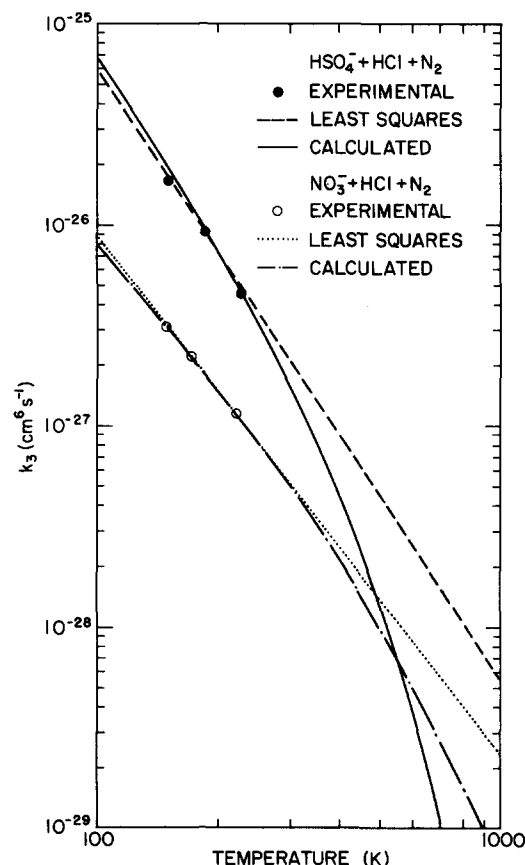

FIG. 1. Rate coefficients for the association reactions of NO_3^- + HCl and HSO_4^- + HCl in a N_2 buffer. The experimental data and least squares curves are from Viggano (Ref. 21) and Viggiano et al., (Ref. 22) respectively. The calculations were normalized to the data at 200 K.

to the experimental data, and the temperature dependences calculated using Eq. (13) for the two reactions. The calculated temperature dependences were normalized to the data at 200 K. The vibrational frequencies for the ions were calculated ab initio by Deakyne and are listed in the Appendix.[42]

As can be seen in Fig. 1, the temperature dependence is fit extremely well over the range of the experimental data. For NO_3^- clustering to HCl the temperature dependence can be expressed approximately as $T^{-2.5}$ at temperatures less than 300 K. This is the same result as if vibration were ignored [Eq. (10)]. The simple calculation based on Eq. (12) predicts the larger temperature dependence found for the HSO_4^-–HCl system very well. The larger temperature dependence is a consequence of HSO_4^- having a vibrational frequency of 136 cm^{-1} ($= 197$ K).[42]

From the form of Eq. (12) another obvious conclusion is that the description of the temperature dependence by a single T^{-n} dependence can quickly break down. This is shown graphically in Fig. 1. At low temperatures only a slight difference between the experimental least-squares line and the calculated temperature dependence is found. At temperatures above 300 K, large discrepancies between the curves appear for both systems. In fact, the discrepancy for the HSO_4^-–HCl system becomes a factor of 15 at 700 K. Due to the higher vibrational frequencies of NO_3^- (compared to HSO_4^-) this effect is not as pronounced in the NO_3^-–HCl system although still important. One must therefore be very cautious when extrapolating rate coefficients of ion–molecule association reactions to temperatures outside the experimental data range. This effect is more important when extrapolating to higher temperatures but for some systems will also be important in extrapolating to lower temperatures. The temperature where nonlinearity becomes important is highly system dependent since the nonlinearity depends on the vibrational frequencies of the reactants.

In order to show this importance, least squares fits to T^{-n} dependences were made at 50 K intervals for the above systems for the calculated temperature dependence. The results are listed in Table I. For the HSO_4^-–HCl system the calculated value of n varies from 3 in the 100–150 K tem-

perature range to 7.6 in the 750 to 800 K range.

Phase space theory calculations for the associations of $C_6H_6^+$ and $CH_2CF_2^+$ to their respective parent neutrals[19] have previously found T^{-n} dependences that vary with temperature. In Fig. 2, the experimental results and phase space theory calculations of Liu et al. are compared to the present theory for the association of $C_6H_6^+$ with C_6H_6 in a C_6H_6 buffer. The vibrational frequencies used by Liu et al.[19] were used in the present study (these are listed in the Appendix) so that a direct comparison can be made. The present calculations were normalized to the phase space theory calculations at 250 K. Good agreement between the two theories is evident. The present calculations give only a slightly steeper temperature dependence. This indicates that the temperature dependence calculated in phase space theory is also mainly due to the temperature dependences of the rotational and vibrational partition functions. In fact, the present calculations agree somewhat better with the experimental results for this example. Calculations based on Eq. (13) for $CH_2CF_2^+$ clustering to its parent neutral yields similar agreement. In this case phase space theory results are in slightly better agreement with the experimental results.

Phase space theory calculations were made in which vibrations were ignored and temperature dependences were found that agreed with those given by Eq. (10).[18] Therefore, if one is interested in only the temperature dependence of ion–molecule association reactions in the low pressure limit, it is much easier to use either Eq. (13) or (14) than phase space theory and obtain results that appear to be equally good.

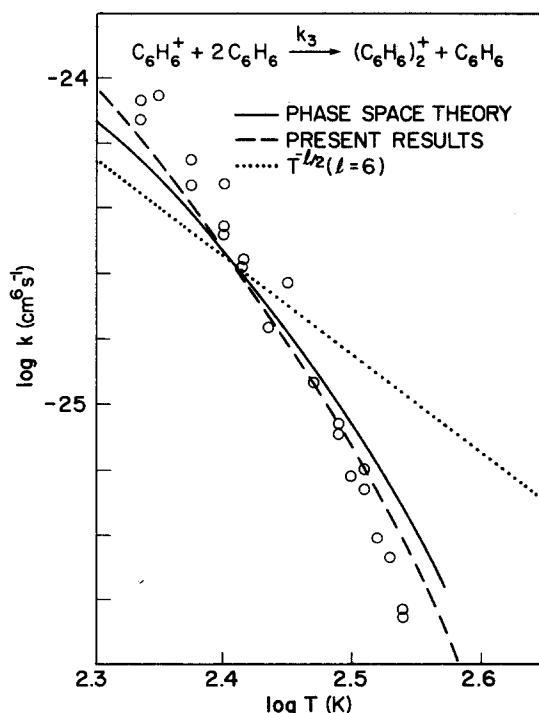Also included in Fig. 2 is a line corresponding to a T^{-3}

TABLE I. Calculated T^{-n} dependences for the reactions of $NO_3^- + HCl$ and $HSO_4^- + HCl$.

Temperature range (K)	n for $NO_3^- + HCl$	n for $HSO_4^- + HCl$
100 – 150	2.51	2.98
150 – 200	2.54	3.31
200 – 250	2.62	3.71
250 – 300	2.75	4.12
300 – 350	2.91	4.54
350 – 400	3.10	4.96
400 – 450	3.30	5.36
450 – 500	3.51	5.74
500 – 550	3.69	6.09
550 – 600	3.90	6.44
600 – 650	4.07	6.75
650 – 700	4.27	7.06
700 – 750	4.44	7.33
750 – 800	4.59	7.61

FIG. 2. Rate coefficients for the association of $C_6H_6^+$ to C_6H_6. The circles represent the experimental data of Liu et al. (Ref. 19). The solid line represents phase space theory calculations (Ref. 19). The dashed line represents the present calculations normalized at 250 K. The dotted line represents calculations to the Herbst (Ref. 3) and Bates (Ref. 8) theory in which vibrations have been ignored.

dependence. This temperature dependence is what is expected for the case in which vibrations have been neglected. Again a huge difference is apparent between this line and the curves from the present calculations or phase space theory, both of which include vibration.

The above discussion has neglected the effect of temperature on the collisional stabilization step. While this dependence is usually small, it is often nonnegligible. Information on this step can be obtained from comparing the experimentally measured temperature dependence to the calculation of the temperature dependence of the equilibrium constant [Eq. (12)].

Evidence for a temperature dependence in the collisional stabilization step comes from comparing results obtained in different buffers. Frequently results obtained in different buffers show appreciably different temperature dependences. This difference was observed for the association of N_2^+ to N_2 in helium and nitrogen buffers. Böhringer *et al.*[31] found approximately a $T^{-0.6}$ more negative temperature dependence in a He buffer than in a N_2 buffer. Smith *et al.*[37] explained this as indicating different mechanisms for cluster stabilization in the two buffers. They concluded that the N_4^+ complex was stabilized by V–T energy transfer in the He buffer and by ligand switching in the N_2 buffer. Since the latter process could be expected to be equal to the collision limit and therefore temperature independent, Smith *et al.*[37] postulated that all the difference in the temperature dependences was due to the temperature dependence of the collisional stabilization step in He.

We have previously found[21,22] different temperature dependences in different buffers for NO_3^- and HSO_4^- clustering to HCl. We also found significantly steeper temperature dependences in a He buffer than in N_2 or H_2 buffers. Table II lists the temperature coefficients to least squares fits to T^{-n} dependences (over the limited range of the data, T^{-n} dependences describe the data adequately) to the experimental data for these reactions in the different buffers. For HSO_4^- clustering to HCl, the temperature dependence in N_2 and H_2 buffers was essentially the same with the temperature dependence for He being about $T^{-0.6}$ more negative. In the case of NO_3^- clustering to HCl, the temperature dependence in the H_2 buffer was $T^{-0.57}$ less negative than in a N_2 buffer and than in a He buffer $T^{-0.9}$ more negative than in a N_2 buffer. The calculations for HCl clustering to NO_3^- and HSO_4^- as well as that for the N_4^+ system are in good agreement with the experimental value for the N_2 buffer in all three cases discussed above. This seems to indicate that in a N_2 buffer there is little or no temperature dependence in the collisonal stabilization step. On the other hand, data taken in a He

buffer show a larger temperature dependence than predicted by Eq. (12) by an amount varying between $T^{-0.3}$ and $T^{-0.9}$. Assuming the temperature dependence in a N_2 buffer really is negligible, one concludes that the additional temperature dependence in the He buffer is due to the collisional stabilization step.

Various attempts have been made to predict the temperature dependence of the collisional stabilization step for a monatomic buffer. Patrick and Golden[14] as well as Herbst[4] estimate a dependence between T^0 and T^{-1}. Bates[8] predicts between a $(\theta + T)^{-3/2}$ (in the limit of high θ this is T^0) and $T^{-3/2}$ dependence, where θ is a constant. The magnitude of the temperature dependence of the collisional stabilization step in He for the systems discussed above is in the ranges given by these theories.[4,8,14] Phase space theory does not address the temperature dependence of the collisional stabilization step, however, users of phase space theory often assume this step is temperature independent.[15–20] This does not seem to be a reasonable assumption since different buffers give different temperature dependences. The limited amount of data taken in a H_2 buffer indicates that the temperature dependence of the collisional stabilization step is also small in this case. The indication of a $T^{+0.5}$ dependence in the NO_3^-–HCl system seems out of line since it represents a negative value of δ and may indicate either an error in this data or something that is not explainable at present.

Only qualitative arguments can be given to explain the different temperature dependences in the different buffers. In the case of a He buffer, the collisional stabilization step must involve vibrational to translational energy transfer. In the molecular buffers, vibrational to rotational and vibrational to vibrational energy transfer may also be important. It is possible that V–T energy transfer has a temperature dependence while V–V and V–R energy transfer does not. In any case, it does not appear to be necessary to invoke a ligand switching mechanism as postulated[37] for the N_4^+–N_2 system to explain the absence of a temperature dependence of the collisional stabilization step, although this still remains a likely mechanism.

Adams and Smith[33] have measured the collisional association rate coefficients for a number of neutrals associating with CH_3^+ in a He buffer. These results had been compared to Eq. (10), and δ values in the range -0.2 to 0.9 were found. These are comparable to the values given in the three examples above. The largest value ($\delta = 0.9$) was for CO_2 clustering to CH_3^+ and appeared anomalously large when compared to the other systems. Calculating the temperature dependence according to Eq. (13), one finds a δ value of 0.5 rather than 0.9. Again this is due to the fact that CO_2 has low frequency vibrations.[43] This is in much better agreement with the other values of δ found by Adams and Smith.[33] The calculation again shows that the temperature dependence of the rate constant can not be represented by a T^{-n} dependence over a large temperature range. This has implications when extrapolating the data to the very cold temperatures in interstellar clouds.

Bass and Jennings[18] have applied phase space theory to the data of Adams and Smith.[33] They concluded that all the data could be explained without the use of a δ parameter

TABLE II. Measured T^{-n} dependences for the reactions of NO_3^- + HCl and HSO_4^- + HCl in different buffers (Refs. 21 and 22).

NO_3^- + HCl	HSO_4^- + HCl	Buffer
3.52	3.57	He
2.06	2.95	H_2
2.62	3.06	N_2

(equivalent to stating that the stabilization step has no temperature dependence). This conclusion was based on the fact that, according to the calculations,[18] the measurements of Adams and Smith[33] were not made in the low pressure limit. This can be checked by studying the reaction as a function of pressure and seeing if the effective two body rate coefficient extrapolates to zero in the limit of zero pressure. Adams and Smith[33] have done this check and concluded that they were in the low pressure limit. Taking this into account, the δ value obtained here (0.5) is in good agreement with the examples given above in which nonzero δ values appear necessary to explain the different temperature dependences in different buffers. Thus, it appears necessary to include a temperature dependent stabilization step in He buffers.

Another example in which vibrational participation is important in determining the temperature dependence of association reactions is the association of CH_5^+ with CH_4. Adams et al.[35] measured this rate in a He buffer at 80 and 204 K. Assuming a T^{-n} dependence to their data results in a value for n of 3.4. The present theory gives a value of 3.49, in good agreement with the measurement. Assuming vibrations to be unimportant results in a value for n of 3.

The final example to be discussed here is the reaction of Br^- with WF_6. The reaction proceeds by both association (to form WF_6Br^-) and charge transfer (to form WF_6^-). The rate coefficient for this reaction has been found to be independent of temperature and pressure.[23] In contrast, the branching ratio was found to be highly dependent on both temperature and pressure. Viggiano et al.[23] postulated that the association channel has both radiative and collisional components. The authors extrapolated the branching ratio ([WF_6Br^-]/[WF_6^-]) to zero pressure in order to determine the radiative component. Making the assumption that the lifetime of the complex was determined by dissociation into products (rather than reactants) and noting that the reaction was thermoneutral, they used Eq. (13) to calculate the temperature dependence of the branching ratio. The zero pressure branching ratio was found to be represented by approximately a $T^{-7.25}$ dependence. The calculated dependence at the center of the temperature range was $T^{-7.1}$, in good agreement with the experimental number. Both the experimental data and the calculations showed nonlinearity from the above numbers (although they are useful for comparative purposes). A calculation ignoring vibrations result in a temperature dependence of $T^{-1.5}$. This is the most dramatic example of the importance of vibrations that has been seen to date. The reason for this is that WF_6 has nine vibrational frequencies[43] less than or equal to 322 cm^{-1}. These are listed in the Appendix.

CONCLUSIONS

A simple expression has been derived to calculate the temperature dependences of ion molecule association reactions in the low pressure limit. This expression is based on the work of Herbst[1–5] and Bates[6–11] who made the assumption that the vibrational frequencies of the reactants were such that $h\nu \gg kT$. It has been shown that this limitation can be removed and that these theories have much more general applicability than previously thought.

Several examples are given in which this modified form of the theories of Herbst[1–5] and Bates[6–11] are compared to experiment. In all cases good agreement for the temperature dependence is found between experiment and the modified theory. It is concluded that in cases in which vibrational partition functions are significantly different from 1, it is not possible to represent the temperature dependences of ion molecule association reactions by a single T^{-n} dependence. This has important implications when data are extrapolated outside the range of the experimental data.

The present formulation has been compared to the results of phase space theory. The two calculations are in good agreement although a slight difference between the two theories can be seen. This is readily explainable since the modified thermal theory of Herbst[1–5] and Bates[6–11] and phase space theory differ only in that the latter makes allowance for internal angular momenta of the reactants. This is generally a small effect.[47]

By comparing results in different buffers it has been shown for several systems that the temperature dependence of the collisonal stabilization step is nonnegligible. It appears that in molecular buffers there is just a small temperature dependence in the stabilization step, while for a He buffer approximately a $T^{-0.5 \pm 0.5}$ dependence is observed.

APPENDIX

TABLE A1. Vibrational frequencies used in the calculations in cm^{-1}. Degeneracies in parentheses.

Reference:	42	42	44	19 $C_6H_6 =$ $C_6H_6^+$[a]	42	45	46	43	43
	NO_3^-	HSO_4^-	HCl		CH_3^+	CO_2	CH_3^+	CH_4	WF_6
	724(2)	137	2989	3062	1496	1351	109	2914	771
	873	442		3068	1526(2)	672(2)	1247	1526	671(2)
	1086	449		1326	3199	2396	1440	3020(3)	712(3)
	1402(2)	622		1150	3398(2)		3037	1306(3)	258(3)
		640		995			996	1526	319(3)
		645		849(2)			1218		215(3)
		911		3062(2)			1413		
		1162		1596(2)			1509		
		1208		1310			2055		
		1428		1038(2)			2795		
		1438		992			2933		
		3886		703			2970		
				606(2)					
				3047(2)					
				1486(2)					
				1178(2)					
				1010					
				975					
				673					
				410(2)					

[a]The frequencies of $C_6H_6^+$ were taken to be the same as those of C_6H_6.

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